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http://dx.doi.org/doi:10.21954/ou.ro.0000f0a9

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Development, evaluation and application of protocols for the analyses of trihalomethanes and haloacetic acids in potable water

A thesis submitted for the degree of
Doctor of Philosophy

By

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May 2012

DATE OF SUBMISSION : 31 JANUARY 2012
DATE OF AWARD : 27 FEBRUARY 2013

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DECLARATION

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Imran H. S. Janmohamed

"The man of knowledge is the one who recognises that what is known is very little compared to what is not known, and as a result he considers himself ignorant, and accordingly he increases his efforts to know more by going out in search of knowledge." Ali ibn Abi Talib (600 - 661 AD)

I Abstract

Potable water distribution systems are a dynamic environment requiring constant monitoring of the levels of contaminants, such as trihalomethanes (THMs) and haloacetic acids (HAAs), to ensure a high quality and that the regulatory standards are always met. The monitoring of specific disinfection by-products (DBPs) is not typically continuous as the current industrial practice is manual sample collection, at regular intervals and at known locations, which are then sent to specialist analytical laboratories for analysis.

The aims of this project were to develop, optimise and apply new and existing analytical protocols for the analysis of THMs and HAAs from UK water sources. The project also provided an opportunity to evaluate if the methods were suitable for the analysis of THMs in near-real time (HS-GC-MS and HS-SPME-GC-MS). The early monitoring of THMs would allow any corrective measures to be implemented sooner. The suitability of GC-MS (EI), GC-MS (ECNI), GC×GC-ToFMS and GC-μECD for HAA concentration measurements was also evaluated. Analysis of HAAs by GC×GC-ToFMS in treated water samples have not been reported before. Apart from the GC-MS (EI), the analytical performance of the methods developed were generally equivalent to those used in regulatory laboratories.

HS-GC-MS was then utilised to determine the influence of a series of parameters on the formation potential of THMs in upland and lowland water samples. Similarly, GC-μECD and GC×GC-ToFMS were utilised to determine the formation potential of HAAs. GC-μECD was also applied to the determination of HAA concentrations in treated water samples from geographically different sources in the UK. The total HAA5 concentration across thirteen sites in England had concentrations well below the US regulated levels of 60 μg/l.

II Acknowledgements

Firstly I would like to offer my sincerest and heartiest gratitude to my supervisor, Dr Geraint Morgan, who has supported me throughout my PhD. Without his active encouragement, dedicated effort and meticulous methodology, I would not have been able to complete this research and thesis. I am also grateful to Dr Jon Watson for his knowledge, advice and guidance in this research. I am grateful to my other supervisors, Prof Simon Parsons and Prof Colin Pillinger, for their support and advice.

I wish to thank the sponsoring companies, Yorkshire Water Services and The Open University, that have funded this research based on their strategic objectives.

I would like to thank Diane Turner for her assistance, advice and expertise on this project. I am thankful to the team at Cranfield University, Dr Emma Goslan and Dr Cynthia Bougeard for their assistance in this work. I would like to thank for Dr Andrew Morris for his assistance in the proof reading of this thesis.

To my friends and colleagues at OU and WF for their love and support. In my daily work, I was supported by a group of friendly and cheerful fellow students and peers, who contributed to my personal well-being with excitement and fun.

I would like to thank my family for their undivided support and encouragement throughout the years, it is with all their personal sacrifices, that I have been able to realise this work. Special thanks go to my mother whose love has got me through the tough times. To my brother whose unwavering support I have always felt behind me. To my sister and sister (in law) for keeping my spirits high. To my mother (in law) for her continued support. To my children for being the lights of my eyes and finally to my lovely wife for all the love and inspiration that got me through to the end.

Finally, I would like to dedicate this work to my late father, Shabbir Janmohamed, whose love and support for my education has been selfless, and whose absence and pearls of wisdom are missed in my life.

III Collaborative Partners

This research project was jointly funded by Yorkshire Water Services Ltd and The Open University through the matched-funded studentship initiative. This research was based on Yorkshire Water's strategic focus of providing high quality water and wastewater services, and The Open University's strategic interest in undertaking joint collaborative ventures with industrial partners to facilitate effective knowledge transfer.

Yorkshire Water provide water and wastewater services to more than 4.7 million people and 140,000 businesses in the Yorkshire and the Humber region of England. They provide high quality water equivalent to 1.3 billion litres a day. They also collect, treat and dispose of about 1 billion litres of wastewater back into the environment every day. Yorkshire Water operate more than 700 water and sewage treatment works, 120 reservoirs and 40,000 miles of water and sewerage mains. Yorkshire Water is the principal subsidiary of Kelda Group, a British utility company based in Bradford. Kelda Group was formally a listed London Stock Exchange Company, but was privatised in 2008. For the financial year 2011, Kelda Group had a revenue of £ 950 million, with post-tax profits of £ 59.8 million.

This research was undertaken within the Department of Physical Sciences at The Open University, in collaboration with the Cranfield Water Science Institute at Cranfield University, who are internationally recognised for their research, education and expertise in the field of water and sanitation, water policy, modelling, water and wastewater technology, and risk management for the water sector.

In addition to financial support, Yorkshire Water Services Ltd. also provided advice and confidential data from their distribution system, which enabled the author to analyse the temporal variations in THM concentrations and other parameters relevant to their formation (Chapter 2).

Cranfield University provided all the real water samples and undertook the extraction and derivatisation of the haloacetic acids in the samples, which were then used to develop and optimise the instrument analysis methods (Chapter 5). They also performed the formation potential experiments for the THMs and HAAs in treated UK waters (Chapter 6), and were partners in the study of HAA concentrations in various geographical locations across England (Chapter 7).

IV Nomenclature

1D-GC	One dimensional - gas chromatography
2D-GC	Two dimensional - gas chromatography
AWWA	American Water Works Association
BCAA	Bromochloroacetic acid
BDCAA	Bromodichloroacetic acid
CE	Capillary electrophoresis
$CHBr_3$	Tribromomethane (or bromoform)
$CHCl_2Br$	Bromodichloromethane
$CHCl_3$	Trichloromethane (or chloroform)
$CHClBr_2$	Dibromochloromethane
CI	Chemical ionisation
CU	Cranfield University
DBAA	Dibromoacetic acid
DBCAA	Dibromochloroacetic acid
DBPs	Disinfection by-products
DCAA	Dichloroacetic acid
DEFRA	Department for Environment, Food and Rural Affairs
DOC	Dissolved organic carbon
DWI	Drinking Water Inspectorate
EI	Electron impact ionisation
ESI	Electrospray ionisation
ECNI	Electron capture negative chemical ionisation
FAIMS	Field asymmetric waveform ion mobility spectrometry
GC	Gas chromatography
GC×GC-ToFMS	GC×GC - time of flight mass spectrometer
GC-μECD	Gas chromatography - micro electron capture detector

GC-MS	Gas chromatography - mass spectrometry
HAAs	Refers to either HAA5 or HAA9
HAA5	Five specific haloacetic acids (MCAA, MBAA, DCAA, TCAA and DBAA)
HAA5*	Five specific haloacetic acids (MBAA, DCAA, TCAA, BCAA and DBAA)
HAA6	Six specific haloacetic acids (MCAA, MBAA, DCAA, TCAA, BCAA and DBAA)
HAA9	Nine specific haloacetic acids (MCAA, MBAA, DCAA, TCAA, BCAA, DBAA, DBCAA, BDCAA and TBAA)
HANs	Haloacetonitriles
HCl	Hydrochloric acid
HOBr	Hypobromous acid
HOCl	Hypochlorous acid
HPI-A	Hydrophilic acid fraction
HPLC	High pressure liquid chromatography or High performance liquid chromatography
HS	Headspace
IARC	International Agency for Research on Cancer
IC-MS	Ion chromatography-mass spectrometry
ICP	Inductive coupled plasma
IRIS	Integrated Risk Information System (USEPA)
IS	Internal standard
LC	Liquid chromatography
LLE	Liquid-liquid extraction
LLME	Liquid-liquid micro extraction
LOD	Limits of detection
m/z	Mass to charge ratio
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MS	Mass spectrometry

MTBE	Methyl tertiary butyl ether
MW	Molecular weight
MX	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
NCI	Negative chemical ionisation
NOM	Natural organic matter
Ofwat	The Water Services Regulation Authority (formerly Office of Water Services)
OU	The Open University
PCI	Positive chemical ionisation
PSSRI	Planetary and Space Sciences Research Institute
SIM	Selected ion monitoring
SPE	Solid phase extraction
SPME	Solid phase micro extraction
TBAA	Tribromoacetic acid
TCAA	Trichloroacetic acid
THMs	Trihalomethanes - refers to the four trihalomethanes ($CHCl_3$,$CHCl_2Br$, $CHClBr_2$, $CHBr_3$)
THM4	Four specific trihalomethanes ($CHCl_3$,$CHCl_2Br$, $CHClBr_2$, $CHBr_3$)
ToF	Time of Flight
TTHMs	Total trihalomethanes - Summation of the four trihalomethanes ($CHCl_3$,$CHCl_2Br$, $CHClBr_2$, $CHBr_3$)
UP	Ultrapure
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
YWS	Yorkshire Water Services Ltd

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1. Introduction

1.1 General introduction

The need to have clean and contaminant-free drinking water and high quality wastewater services are of paramount importance to the personal well-being of humans as well as the environment. The United Nation's World Health Organisation (WHO) has set basic water guidelines, which are the basis for EU, UK and US legislation. An established goal of the WHO and its Member States relating to drinking water is: *"All people, whatever their stage of development and social and economic condition, have the right to have access to drinking water in quantities and of a quality equal to their basic needs"* (UN).

In the United Kingdom, water companies are involved in the collection, treatment and supply of more than 16 billion litres of water to domestic and commercial customers everyday. They are also responsible for the daily collection of over 10 billion litres of the resulting wastewaters and returning it safely to the environment following treatment. The primary areas of investment for the water industry, therefore, falls into four main categories (Website - Water UK, 2011):

- improving drinking water and environmental quality to maintain legislative and customer requirements;
- enhancing the efficiency of the water treatment plants and water distribution system ensuring minimum costs;
- ensuring the infrastructure for the supply of clean water and the removal of wastewater is fit for purpose; and
- ensuring a satisfactory balance between supply and demand of water.

In order to meet regulatory requirements, the UK water industry analyses specific contaminants in drinking and wastewater systems. These analyses should be completed in an accurate, precise, cost effective and timely manner.

The potable water system is a dynamic environment, requiring constant monitoring to ensure the highest quality and that regulatory standards are met. The need to monitor continuously the levels of contaminants, such as disinfection by-products (DBPs), is important because of a number of transformations that organic compounds can undergo in water (Biziuk *et al.*, 1996; Idornigie *et al.*, 2010). The monitoring of specific DBPs is not typically continuous in potable water distribution systems, therefore valuable data that could be used to understand DBPs formation and removal are not readily available (Brown *et al.*, 2006). The current industrial practice is manual sample collection, at regular intervals and at known locations, which are then sent to specialised central analytical laboratories for offline analysis. This practise is labour intensive, time consuming and a potentially costly venture. Geme and colleagues concluded that new analysers are needed to provide data on the concentrations in real time or near-real time, particularly for DBPs in water (Geme *et al.*, 2005). Real time in this thesis is defined as the ability to obtain representative analytical information from the potable water distribution systems directly and instantaneously (e.g. water temperature measurement). Near-real time analysis is defined in this thesis as a measurement that requires further processing of the sample (e.g. separation by gas chromatography) prior to a result being obtained. This introduces a time delay, usually several minutes, before any suitable information can be available for the decision making process. Such systems would be important, as they would provide valuable information at an early stage allowing corrective measures to be implemented much sooner than they are currently via offline analyses.

The most abundant DBPs in potable water, formed by the disinfection process, are trihalomethanes (THMs) and haloacetic acids (HAAs). Both families of compounds are toxic and hence their total concentrations are regulated in the US (USEPA, 1998b). THMs are volatile and sparingly soluble in water and as a result are an ideal candidate for near-real time analysis. HAAs are non volatile and require complex sample preparation and derivatisation prior to chromatographic analyses. As a result, only THM concentrations are regulated in the UK (DWI, 2010c), and only one study of the HAA concentrations in

treated UK waters had been published at the start of this research (Malliarou *et al.*, 2005). However, HAAs are considered as high priority compounds for potential regulation in the near future (Fawell *et al.*, 2002), and are listed for future regulation in the EU Water Directive (Cortvriend, 2008). In order to prepare for this regulation, water companies are taking a proactive approach to assess the most appropriate methodology for the analysis of HAAs in their water samples. In 2011, Marshall reported that the European Commission will not hold any formal review of the Drinking Water Directive. This would suggest that any incorporation of HAAs levels within the Directive would not be implemented for at least another four years (Marshall, 2011).

1.2 Thesis overview

The overall aim of this project was to develop, optimise and evaluate new and existing analytical protocols for the analysis of THMs and HAAs from UK water sources. The analytical work was conducted with existing commercial instrumentation to evaluate their suitability for the analyses of these contaminants. Once optimised, the performance of these methods were evaluated using treated water samples. They were then utilised to determine the influence of a series of parameters on the formation potential of THMs and HAAs in upland and lowland water samples and then applied to the analysis of treated water from geographically different sources in the UK.

The potential to analyse THMs in real or near-real time provided an additional focus to the requirements for the analytical methods evaluated. Specifically, these requirements included the desire to find an alternative to the existing analytical methods that utilise purge and trap or liquid-liquid extraction and an electron capture detector; thereby precluding the analysis of THMs outside of conventional analytical laboratories, as these methods would be impractical for real or near-real time monitoring of THM levels within the UK water distribution systems.

The work was performed at the Department of Physical Sciences, (formerly Planetary and Space Sciences Research Institute (PSSRI)) at The Open University. PSSRI has been involved in a wide range of research, from the study of the Solar System and the laboratory analysis of extraterrestrial material to the development of instrumentation for international space missions. PSSRI not only develops analytical instruments, based mainly around mass spectrometry, but is also an end-user of such systems and has a track record in developing novel methods. PSSRI also has a history of successfully providing end-to-end solutions to specific challenges and accommodates the necessary resources to design, manufacture and qualify semi-autonomous miniature evolved gas analysers, uniquely tailored for their specific applications.

In order to capitalise on this expertise this PhD project was initiated between The Open University and Yorkshire Water Services Ltd in collaboration with Prof. Simon Parson's group in the Water Science Institute at Cranfield University, to evaluate if suitable analytical methods could be developed for THMs that utilised mass spectrometers as the detector.

A summary of the contents of each thesis chapter is provided below:

- **Chapter 1** provides an overview of: potable water sources; the composition, toxicity, regulatory requirements and formation mechanisms for the DBPs; the analytical methods currently utilised and those proposed for use in the thesis;
- **Chapter 2** provides a detailed analysis of the temporal variance of THM and THM4 concentrations, and other relevant parameters, obtained from the potable water distribution system of Yorkshire Water Services Ltd;
- **Chapter 3** summarises the final experimental methods, chemicals and reagents, and instrumentation for the analysis of THMs and HAAs following their optimisation;
- **Chapter 4** evaluates and optimises existing analytical methods that would be suitable for translation to near real-time monitoring of THM concentrations. The performances

of HS-GC-MS, HS-SPME-GC-MS, HS-GC-μECD and LLE-GC-μECD will be evaluated in terms of their linearity, repeatability, accuracy and LODs, against published methods. A discussion of their viability for near-real time monitoring will also be evaluated along with the criteria that would need to be achieved for regulatory compliance.

- **Chapter 5** investigates whether alternative chromatographic methods (GC-μECD, GC-MS (in electron impact ionisation mode), GC-MS (in chemical ionisation mode) and comprehensive chromatography (GC×GC-ToFMS)) are suitable for the analysis of HAAs. The research also investigates the influence of instrument parameters on the performance of the analyses.
- **Chapter 6** determines the influence of various disinfection parameters on the formation of THMs and HAAs, under controlled laboratory conditions. It also evaluates if THM concentrations could be used as a surrogate for HAA concentrations in UK waters and the suitability of two analytical methods (GC-μECD and GC×GC-ToFMS) for the measurement of HAA concentrations in treated water samples.
- **Chapter 7** determines the concentrations of each of the nine HAAs, the total concentration of the nine HAAs (HAA9) and the US regulated HAA5, from thirteen sites within five water utility companies, across England.
- **Chapter 8** has the concluding remarks and suggestions for future work.

The majority of the literature review in this Chapter was conducted primarily between January 2006 - September 2010.

1.3 Global water sources and demand

Most (up to 97.5 %) of the water on Earth is saline, with only 2.5 % being freshwater. Seventy five percent of this freshwater is distributed as ice caps and glaciers, 24 % can be found underground and only 1 % is present in lakes, rivers and soil (Gray, 1994). The hydrologic cycle is of great importance to the ecological, environmental and climatic

conditions of an area, and impacts on the condition and availability of potable water. This, in turn, influences the economic and geopolitical status of an area. Potable water is defined as any water that is of the quality suitable for drinking, whether it is used as such or not (WHO, 2006).

Collins *et al.*, (2009) estimated that the demand for water across Europe, in 1995, was around 326 km^3/year and, on average, 44 % of the water abstracted was used for cooling during energy production; 24 % was used for agriculture; 21 % for public water supply and 11 % for industrial use. They also reported that the demand for water also has time variability with annual, weekly and daily cycles. This ever changing water demand is a key parameter in any company's ability to provide a continuous supply of clean water, and has strong implications on the water treatment plants and processes employed (Parsons *et al.*, 2006b).

The required water supply systems are for the collection, transmission, treatment, storage and distribution of water from source to consumers' (UN, 1997). A simple water supply system consists of three subsystems, abstraction, treatment, and distribution. Once 'raw water' is abstracted and treated, it is then supplied either directly to the end user through distribution pipes or transferred to water tanks / service reservoirs for storage before distribution. These storage locations provide a constant supply of water during the fluctuating diurnal water demand.

1.4 Sources of potable water

The two main sources of potable water are surface and ground water. However, other options of obtaining potable water include desalination, bulk water transfer and melting of natural ice (Gray, 1994). Recycled or reclaimed water, which is sewage water after appropriate treatment, can be used for potable purposes, but is most commonly used for non-potable purposes, such as in agriculture, landscape and public parks (USEPA, 2004).

Surface water

This is a term describing any water body found flowing or standing on the surface, such as streams, rivers, ponds, lakes, and reservoirs. It originates from a combination of sources, for example surface runoff, direct precipitation, soil moisture and water table discharge. The quality and quantity of these waters will depend on the climatic and geological factors of the region at that time (Gray, 1994). Around 70 % of drinking water in England and Wales has been derived from surface waters and their organic content can be highly variable (DEFRA, 2006).

Ground water

This is a term describing any water found beneath the Earth's surface, often located between the saturated soil and rock. Aquifers, the source that supplies wells and springs, are only found in selected locations. The discovery of these aquifers is critical before any water can be abstracted to the surface and purified. Water obtained from this source is generally of higher quality, usually requires minimal treatment, and hence is cheaper to use (Gray, 1994; Whitaker *et al.*, 2003). In England and Wales, ground water accounts for 33 % of the potable water and generally contain low levels of organic matter, but may include a high bromide content (DEFRA, 2006; Whitaker *et al.*, 2003).

1.5 Potable water treatment

Water treatment is any process used to remove existing components from water to make it suitable for subsequent use. This could be for a wide range of applications including drinking, industrial processes, medical and environmental discharge.

Potable water treatment involves the use of treatment techniques to purify water to a degree suitable for human consumption, providing a continuous and adequate supply of water that is chemically and microbiolically acceptable and aesthetically pleasing (Gray, 1994). Substances that are removed during the process of drinking water treatment

include bacteria, algae, viruses, fungi, minerals such as iron and sulphur, natural and man-made chemical pollutants, and natural organic matter (Parsons *et al.*, 2006b).

The treatment of water can generally be divided into three principle stages: primary (solid removal), secondary (fine solid removal) and tertiary treatment (disinfection and conditioning) and involves many physical, chemical and biological processes. These processes include screening, storage, aeration, coagulation, flocculation, sedimentation, filtration and finally disinfection, both primary and secondary (Parsons *et al.*, 2006b). Other processes include sludge disposal, regeneration, softening and chemical conditioning (AWWA, 2003).

1.6 Regulatory bodies

As a result of the importance of maintaining the quality and the affordability of clean drinking water, the public water services are monitored and controlled by government-appointed regulators who set legally-binding standards. These bodies, which maintain and report the progress against the regulations, are important in providing guidance to the water companies and population at large. Regulations are focused in four main areas: drinking water quality, environmental, economic, and health and safety (Website - Water UK, 2011).

1.6.1 Drinking water quality regulations in the UK

The Drinking Water Inspectorate (DWI), in England and Wales; the Drinking Water Quality Regulator, in Scotland; and the Northern Ireland Environment Agency, are independent government agencies that regulate and assess the public water supplies to ensure it is safe to drink. These agencies monitor the thousands of tests for drinking water quality carried out by the water companies to ensure that they meet the highest EU and UK standards. They also carry out their own inspection to confirm the results provided by the companies.

1.6.2 Environmental quality regulations

The Environment Agency, in England and Wales; the Scottish Environment Protection Agency (SEPA), in Scotland; and the Department of the Environment, in Northern Ireland, ensure that the natural environment is protected. These bodies regulate the amount of water taken from the environment (*via* abstraction) and monitor the quality of effluent placed into the watercourses. The water companies must also show compliance to several governmental organisations such as the Department for Environment Food and Rural Affairs (DEFRA), and the relevant District Health Authorities and local authorities.

The European Directive, which has been incorporated in the Water Supply (Water Quality) Regulations 2000 (England) and 2001 (Wales), prescribes standards for the quality of water intended for human consumption (EECD, 1997). There are 28 mandatory standards for chemical and microbial contaminants, a further 20 non-mandatory standards covering physical, chemical and microbial contaminants and the mandatory radioactivity parameters, which are all summarised in Appendix 1 (Parsons *et al.*, 2006b). The water legislation is regularly amended as new research on the occurrence and potential hazards of contaminants becomes available.

1.6.3 Economic regulations

The Water Services Regulation Authority (Ofwat) in England and Wales; the Water Industry Commission for Scotland, in Scotland; and The Utility Regulator in Northern Ireland are the economic regulators of the water and sewerage industry. The economic regulations maintain the pricing of waste and potable water as well as financial operations and standards of service of the water companies.

1.6.4 Health and safety regulations

The Health and Safety Executive for Northern Ireland and the Health and Safety Executive in Britain are public bodies that are responsible for the encouragement, regulation and enforcement of workplace health, safety and welfare.

1.7 Water pollutants - Disinfection by-products (DBPs)

Water pollutants come from a variety of sources but fall into two main categories: point (definitive point of entry) and non-point (diffused entry with no direct point of entry) sources (Hill, 2004). They can originate from natural sources or human activities and can have a negative impact on the recipients of the water. Water pollutants can be further divided into physical, radioactive, inorganic and organic pollutants. The organic pollutants can be further subdivided into natural (*e.g.* chemicals from natural degradation and volcanic eruption) and anthropogenic (*e.g.* pesticides used in agriculture) (Biziuk *et al.*, 1996).

Disinfection is a vital process for the treatment of drinking water to prevent the spread of water-borne diseases. Disinfection by-products (DBPs) are a group of organic and inorganic compounds formed as a consequence of the disinfection process by the reaction of disinfectants (such as chlorine) with natural organic matter (NOM) and inorganic substances (such as bromide) that are already present in the water. There are also other natural and anthropogenic sources of some compounds, which have been classified as DBPs (Laturnus *et al.*, 2002; McCulloch, 2003). DBPs such as chloroform have been detected in ice, snow, rain water, fog, air, sea water, fresh water and biological matrices (Watts *et al.*, 2004).

There are just over 500+ DBPs identified but Richardson has also reported that there are also many 'missing' DBPs found in water (Richardson, 2003b). The toxicity and concentration data for many of these DBPs remain relatively limited (Richardson *et al.*,

2007). Richardson *et al.*, (2003b) stated that the four main categories of DBPs of greatest concern, especially in the USA, because of legislative requirements, toxicity data and concentrations levels were: the organic trihalomethanes (THMs), haloacetic acids (HAAs), and the inorganic chlorite and bromate. This thesis will only focus on THMs and HAAs which are of primary interest to the funding organisation.

1.7.1 The major disinfection by-products

Trihalomethanes (THMs)

In the 1970's, THMs were the first group of DBPs identified in drinking water (Rook, 1974). THMs generally represent the most abundant group of DBPs in most drinking water systems (Krasner *et al.*, 1989; Singer *et al.*, 2002). With various combinations of chlorine, bromine and iodine, a theoretical total of 27 THMs could potentially be formed (Xie, 2003). However, there are four main THMs found in drinking water. These are trichloromethane ($CHCl_3$, commonly called chloroform), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and tribromomethane ($CHBr_3$, commonly called bromoform). These THMs are volatile and sparingly soluble in water. The names, chemical formula and physicochemical properties of THMs have been summarised in Appendix 1.

Chloroform was the first DBP to be identified in chlorinated drinking waters and, it is the most abundant THM reported in most drinking waters (Kuo *et al.*, 1997; LeBel *et al.*, 1997; Ristoiu *et al.*, 2009).

Halogenated acetic acids (HAAs)

Halogenated acetic acids are commonly referred to as haloacetic acids or HAAs and broadly represent the second most abundant group of DBPs found in disinfected drinking water (Krasner *et al.*, 1989; Singer *et al.*, 2002). There are nine commonly occurring HAAs which are: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA),

bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TBAA). They are non-volatile and highly soluble in water. The physicochemical properties of HAAs along with their methyl esters, have been summarised in Appendix 1.

Other DBPs

There are several other groups of DBPs, such haloacetonitriles (HANs), haloacetones, halonitromethanes (HNMs), haloketones (HKs), haloaldehydes, halopropanones, cyanogen halides, halofuranones such as MX (3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone) and analogues of MX (Golfinopoulos and Nikolaou, 2005; Sadiq *et al.*, 2004; Xie, 2003). There are several other DBPs that are formed by ozonation and chloramination processes (Xie, 2003). These compounds are typically less of a risk then THMs and HAAs, because they are normally found at lower concentrations and only in a few locations (Richardson, 2003a).

1.7.2 Toxicity of THMs and HAAs

Toxicity evaluation consists of hazard identification, dose response assessment, exposure assessment and risk characterisation (Boorman *et al.*, 1999). DBPs such as THMs and some HAAs have been evaluated to a greater extent while other DBPs are yet to be evaluated owing to their low concentrations in the water system (Richardson, 2003a).

THMs and HAAs have been found to have toxic, carcinogenic and mutagenic effects (Graves *et al.*, 2001; Nieuwenhuijsen *et al.*, 2000; Reif *et al.*, ; Wright *et al.*, 2004). Several epidemiological studies have associated human consumption of drinking water containing THMs and HAAs, to an elevated risk or positive association for cancers of the bladder, lung, rectal, kidney, oesophagus, brain and colon, as well as adverse reproductive effects (Boorman *et al.*, 1999; Cantor, 1997; Koivusalo *et al.*, 1994; Yang *et al.*, 1998; Zierler *et al.*, 1988).

Several studies have shown a significant association between elevated THM concentrations and still births, congenital malformations, birth defects, fetal growth retardation, menstrual cycle irregularities and retarded or low birth weights (Chisholm *et al.*, 2008; Hwang *et al.*, 2008; Hwang *et al.*, 2002; Klotz *et al.*, 1999; Magnus *et al.*, 1999; Nieuwenhuijsen *et al.*, 2008; Toledano *et al.*, 2005; Windham *et al.*, 2003; Wright *et al.*, 2003; Wright *et al.*, 2004). However, in a recent review by Hrudey (2009), it was reported that the THMs and HAAs do not pose a significant risk in comparison to the other DBPs that may be from 1000 to 10,000 times more toxic than the THMs or HAAs (Hrudey, 2009).

An examination of the literature on the cytotoxicity, genotoxicity and mutagenicity of some THMs and HAAs has been summarised in Table 1.1. Brominated HAAs are more cytotoxic and genotoxic than their chlorinated analogues (Nobukawa *et al.*, 2001; Plewa *et al.*, 2002) and iodinated THMs and HAAs are significantly more toxic than their chlorinated and brominated counterparts (Plewa *et al.*, 2010). The overall influence of THMs and HAAs correlates strongly with the concentration consumed (Shaw *et al.*, 2003). Studies have also reported that there are many nitrogenous DBPs (e.g. haloacetamides) that are significantly more cytotoxic and genotoxic than THMs and HAAs (Plewa *et al.*, 2011).

Table 1.1: The relative toxicity of some of the common THMs and HAAs reported in literature.

Type of toxicity	Rank order	Reference
Cytotoxicity	MBAA >> MX > DBAA > MCAA > TBAA > DCAA > TCAA.	(Plewa *et al.*, 2002)
	MIAA > MBAA > TBAA > DBCAA > DIAA > DBAA > BDCAA > BCAA > MCAA > BIAA > TCAA > DCAA	(Plewa *et al.*, 2010)
Genotoxicity	MBAA >> MX > MCAA > DBAA > TBAA DCAA and TCAA did not show any effect.	(Plewa *et al.*, 2002)
	MIAA > MBAA > MCAA > DBAA > DIAA > TBAA > BCAA > BIAA > DBCAA. DCAA, TCAA, and BDCAA were not genotoxic.	(Plewa *et al.*, 2010)
Mutagenicity (with cytotoxicity)	MX > MBAA > DBAA > DCAA > MCAA, TBAA, TCAA $CHCl_3$ and $CHBr_3$ did not show any effect.	(Kargalioglu *et al.*, 2002)

Cytotoxicity is the ability of producing a toxic effect on cells; mutagenicity is the ability to increase the frequency of mutation on an organism; and genotoxicity is the ability to induce DNA damage in cells. MIAA - monoiodoacetic acid, DIAA - diiodoacetic acid, BIAA - bromoiodoacetic acid.

The International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency's Integrated Risk Information System (USEPA IRIS) have classified the four THMs and two HAAs (DCAA and TCAA) for their carcinogenic risk to humans (IARC, 2009; USEPA, 2011), as reported in Table 1.2. $CHClBr_2$, $CHBr_3$ and TCAA are not classifiable as to its carcinogenicity to humans whilst the others are possible carcinogens. The other HAAs have not been classified to date.

Table 1.2: The carcinogen risk classification for the four THMs and two HAAs by USEPA-IRIS and IARC.

Class	Compound	IARC Group	EPA-IRIS Group
THMs	$CHCl_3$	2B	B2
	$CHCl_2Br$	2B	B2
	$CHClBr_2$	3	C
	$CHBr_3$	3	B2
HAAs	DCAA	2B	B2
	TCAA	3	C

The IARC classification is as follows:
Group 1: The agent is carcinogenic to humans,
Group 2A: The agent is probably carcinogenic to humans,
Group 2B: The agent is possibly carcinogenic to humans,
Group 3: The agent is not classifiable as to its carcinogenicity to humans,
Group 4: The agent is probably not carcinogenic to humans.

The USEPA - IRIS classification is as follows:
Group A: Human carcinogen,
Group B1: Probable human carcinogen (sufficient animal and limited human evidence),
Group B2: Probable human carcinogen (sufficient animal and no human evidence),
Group C: Possible human carcinogen.

1.7.3 Regulation of DBPs

Of the 500+ DBPs detected, fewer than a dozen are currently regulated (Cancho *et al.*, 2005; Westerhoff, 2006).

The World Health Organisation (WHO) has published guidance values for several DBPs such THMs and HAAs (WHO, 2006). The guideline values for THMs and some HAAs are shown in Table 1.3. The guidance values were generally derived based on parameters such as average adult individual weight of 60 kg, average water consumption of 2 litres/day, tolerable daily intake and epidemiological studies (IPCS, 2004; WHO, 2006). The tolerable daily intake (TDI) is an estimate of the amount of a substance in food and drinking water, expressed on a body weight basis (μg/kg of body weight), that can be ingested over an average lifetime without appreciable health risk.

Table 1.3: Guideline values formulated by the WHO (WHO, 2006).

Class	Compound	Guideline value (µg/l)	Tolerable daily intake (µg/kg)
THMs	$CHCl_3$	300	15
	$CHCl_2Br$	100	n/a
	$CHClBr_2$	100	21.4
	$CHBr_3$	60	17.9
HAAs	MCAA	20	3.5
	DCAA	50	n/a
	TCAA	200	32.5

No values have been reported for the other HAAs.

The EU member states are required to ensure that a total concentration of 100 µg/l of the four THMs are not exceeded in drinking water supply (EECD, 1997; Tokmak *et al.*, 2004). In the UK, the total THM concentration (*i.e.* the sum of the 4 THMs; also defined as THM4) is regulated at a maximum concentration of 100 µg/l, in a single sample, at the customer tap (2000). The necessary frequency of sampling depends on the population of the supply zone and volume of the treatment works, with an annual maximum of 48 samples taken (DWI, 2010b). HAAs are currently not regulated in the UK, they were identified as high priority compounds for future regulation (Fawell *et al.*, 2002), and are listed for future regulation in the EU Water Directive (Cortvriend, 2008). This is because of the limited knowledge of the levels of HAAs in the UK and current methodology for the analysis of HAAs is time-consuming and expensive. Any regulation could have significant implications for the UK water industry (Harman *et al.*, 2011; Jackson *et al.*, 2008). The total concentrations of THMs found in the UK are usually below the regulated levels of 100 µg/l, however the levels of HAAs (MBAA, DCAA, TCAA, BCAA, DBAA and BDCAA) have been detected on average between 35.1 µg/l to 94.6 µg/l with a maximum concentration of 244 µg/l (Malliarou *et al.*, 2005).

Within the US, in 1979, the USEPA initiated regulatory standards of 100 µg/l for THM4, under the Interim Trihalomethane Rule, for water systems serving over 10,000 people (Zhao *et al.*, 2004). In 1998, as part of an amendment to the Safe Water Drinking Act, the USEPA proposed a two-stage regulation of THMs and HAAs. Under Stage 1 Disinfection and Disinfection By-Product Rule, the maximum contaminant levels (MCLs) for the four THMs (THM4) and five HAAs (HAA5 - MCAA, MBAA, DCAA, TCAA, DBAA) were set at a total concentration of 80 µg/l and 60 µg/l respectively (USEPA, 1998b). The Stage 1 compliance was based on a system-wide running average of four quarterly samples for all community water systems (Westerhoff, 2006). Under the Stage 2 Disinfection and Disinfection By-Product Rule, which is currently in force, the MCLs of THM4 and HAA5 remained the same, but compliance was based on a localised running average of four quarterly samples collected at four locations in the distribution system of each plant (USEPA, 2006; Westerhoff, 2006).

Table 1.4 summarises some of the examples of the THMs and HAAs regulatory limits across the world. Currently there are no regulations in many developing countries.

Table 1.4: The THM and HAA regulatory concentrations for various countries across the world.

Country	**THMs (THM4)**	**HAAs (HAA5)**	**Source of information**
US	80 µg/l	60 µg/l	(USEPA, 1998b)
EU	100 µg/l	n/a	(Tokmak *et al.*, 2004)
UK	100 µg/l	n/a	(DWI, 2000)
Australia	100 µg/l	n/a	(Sadiq *et al.*, 2004)
Canada	100 µg/l	80 µg/l	(HC, 2008; Sadiq *et al.*, 2004)
Japan	100 µg/l	n/a	(Nakahara *et al.*, 1997)
Sweden	50 µg/l	n/a	(Kuivinen *et al.*, 1999)
Turkey	150 µg/l	n/a	(Uyak *et al.*, 2007a)

A brief examination of the actual THM4 levels reported at different locations in several countries was undertaken and is reported in Table 1.5. The table confirms previously reported findings that the concentrations of THMs in drinking water greatly varies in different geographic regions (Yoon *et al.*, 2003).

Table 1.5: The THM4 concentrations found in several countries reported in literature.

Location	Average total THMs levels (range)	References
UK, (Yorkshire)	<100 µg/l , n=100	(Parsons *et al.*, 2006a)
Canada, various	39 µg/l (11 - 98 µg/l, n=12)	(LeBel *et al.*, 1997)
China, Hong Kong	61 µg/l (5 - 138 µg/l, n=57)	(Yu *et al.*, 1999)
Greece, Athens	48 µg/l (15 - 82 µg/l, n=88)	(Golfinopoulos *et al.*, 1998)
South Korea, various	~ 30 µg/l (5 - 84 µg/l)	(Kim, 2009)
Romania, various	< 100 µg/l , n=18	(Ristoiu *et al.*, 2009)
Turkey, Istanbul	94 µg/l (75 - 117 µg/l, n=30)	(Toroz *et al.*, 2005)

1.7.4 Mechanisms for the formation of THMs and HAAs

The formation of an individual THM and HAA in drinking water is not because of the direct reaction of chorine with methane, halogenated methanes or acetic acid, but rather as a result of a complex reaction of NOM with chlorine in the presence of bromide ions in water. A general formation reaction is given by Equation 1.1 (Panyapinyopol *et al.*, 2005):

$$NOM + [HOCl] + Br^- \rightarrow DBPs\ (THMs, HAAs, HANs, MX + many\ others) \quad \text{Equation 1.1}$$

The reaction pathways are still relatively unknown because of the heterogeneous nature of the natural organic matter (NOM), which is different at every treatment site (Aysegul, 2003; Boccelli *et al.*, 2003; Xie, 2003). However, model compounds such as resorcinol-, phenol-, aromatic- and aliphatic-type structures have been used in the literature to illustrate the reactions (Chawla *et al.*, 1983; Dickenson *et al.*, 2008). A possible reaction pathway for the cleavesis of resorcinol to chloroform or TCAA is shown in Figure 1.1.

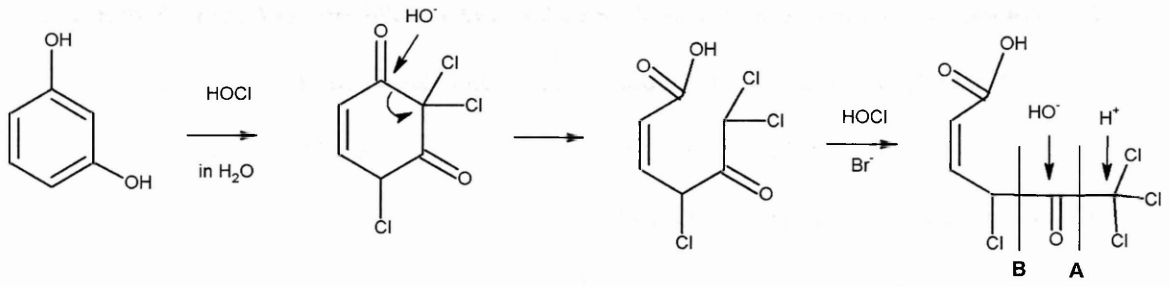


*Figure 1.1: A possible reaction pathway for resorcinol showing a cleavage at **A** will result in the production of chloroform and a cleavage at **B** will form TCAA (adapted from (Rook, 1977)).*

1.7.5 Factors affecting the formation of THMs and HAAs

The quantity of THMs and HAAs formed depend on several factors such as the type and concentration of NOM present, chorine dose, chlorination contact time, pH, temperature and bromide ion concentration (Amy *et al.*, 1998; Carlson *et al.*, 1998; Chang *et al.*, 2008; Cowman *et al.*, 1996; Nikolaou *et al.*, 2004b; Westerhoff, 2006; Xie, 2003; Yang *et al.*, 2007). The influences of a number of these parameters, namely, chlorination contact time, pH, temperature and bromide ion concentrations are presented later in this thesis. However, a brief outline of the influence of those parameters not investigated in this thesis has been summarised here:

1.7.5.1 Influence of Natural Organic Matter (NOM)

NOM is a complex mixture of organic compounds that are generated by physical, chemical and biological activities that are sourced either from allochthonous, *i.e.* entering the water from terrestrial sources, or autochthonous sources, *i.e.* entering the water from biological processes in the water body such as algae, bacteria *etc.* (Bougeard, 2006; Kanokkantapong *et al.*, 2006b). Waters from different locations vary significantly with respect to the concentration and type of NOM precursors present (Gallard *et al.*, 2002). Invariably, the nature and amount of organic matter will determine the type and concentrations of DBPs formed (Yang *et al.*, 2008). The concentrations of dissolved organic carbon (DOC) present in the water have been used to indicate the levels of NOM

present. There are several methods for measuring DOC, however, UV absorbance at 254 nm (UV_{254}) is a simple and useful surrogate measure for DOC (USEPA, 1999).

The major chemical classes of compounds in NOM that are associated with the formation of THMs and HAAs are: humic species, carbohydrates, amino acids, proteins and carboxylic acids (Croué *et al.*, 2000). The resulting magnitude of the quality problems associated with these compounds are presented in the Table 1.6.

Table 1.6: Main chemical classes of compounds found in NOM and associated water quality problems (adapted from (Croué *et al.*, 2000)).

Compounds	DBPs formation (chlorination)	DBPs formation (ozonation)	Biological activities	Colour	Taste and odour
Humic species	major	major	little	major	secondary
Carbohydrates	n/k	n/k	major	none	insignificant
Amino acids	important	mbs	major	major	insignificant
Proteins	important	important	major	major	insignificant
Carboxylic acids	important	n/k	secondary	none	insignificant

Meaning of terms: major - plays a major role, secondary - plays a secondary role, mbs - may be significant, n/k - not known.

NOM includes thousands of organic compounds, making it difficult to evaluate its properties individually. Researchers have attempted to characterise NOM by grouping it into a limited set of categories (fractions or subgroups) based on their characteristics. These independent fractions, isolated from the water samples, will have similar composition and properties, even though their concentrations may be different. A major goal of NOM fractionation and characterisation is to understand and predict the reactivity of each fraction (Croué *et al.*, 2000).

There are several techniques reported in the literature for the fractionation of natural organic matter. Some of the techniques used include adsorption fractionation, evaporation, freeze drying and membrane technologies (Croué *et al.*, 2000; Marhaba *et*

al., 2003; Panyapinyopol *et al.*, 2005). Resin adsorption fractionation is a common technique used to concentrate and categorise organic matter into structurally more specific and physicochemically more analogous fractions. By applying this technique, organics in water can be fractionated into hydrophobic, hydrophilic and transphilic fractions. Each of the three fractions can be further grouped into acids, neutrals and bases. The use of NOM fractions allows the formation patterns of DBPs to be related more directly to the nature of the matter found in different water sources, providing a link to the most appropriate treatment processes (Kanokkantapong *et al.*, 2006a).

1.7.5.2 Influence of the disinfection reagents

Several compounds are used to achieve disinfection. A summary of the main disinfection processes are as follows:

Chlorine gas or hypochlorite solution (chlorination): Chlorination is a relatively simple and low-cost water disinfection process, which uses chlorine gas or hypochlorite solutions as the only disinfectant. It is the most widely used disinfection process (Boccelli *et al.*, 2003; Twort *et al.*, 2000b; WCC, 2008; Yu *et al.*, 1999). Chlorine gas and water react to form HOCl and hydrochloric acid (HCl). In turn, the HOCl dissociates into the hypochlorite ion (OCl^-) and the hydrogen ion (H^+), according to the following reactions (WHO, 2004b).

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \; or \; (HCl)$$ Equation 1.2

$$HOCl \leftrightarrow H^+ + OCl^-$$ Equation 1.3

In order to achieve adequate disinfection, chlorine levels in the drinking water need to be in excess (termed as residual chlorine) to prevent the re-growth of harmful microbial agents during the transfer process to the end user. Chlorine in the form of HOCl and OCl^- is referred to as free chlorine (Kim *et al.*, 2002).

The WHO has established a guideline value of 5 mg/l of residual chlorine in drinking water. The WHO also recommends a residual free chlorine concentration of at least 0.5 mg/l after a contact time of 30 minutes at pH < 8 (Twort *et al.*, 2000b; WCC, 2008; WHO, 2006). The water companies in the UK are required to analyse the residual chlorine in the water treatment works, in service reservoirs and at consumer's taps, although the value for residual chlorine is not regulated (DWI, 2000). Generally, the levels of total free chlorine in waters are found to be at 0.2 - 1 mg/l across the world (Galal-Gorchev, 1996).

Chlorine gas and ammonia (chloramination): Chloramination is another disinfection process that uses chlorine gas, this time in conjunction with ammonia. This process has gained prominence in recent years because it is reported to reduce the formation of THMs and HAAs in the waters during disinfection (Guay *et al.*, 2005). However, some recent studies have shown this process leads to an increase in the formation of other DBPs which are yet not regulated (Yang, 2007; Yang, 2008).

Other disinfection reagents and processes: Some of the other disinfection reagents used are ozone, chlorine dioxide and hydrogen peroxide (Chang *et al.*, 2000a; Chang *et al.*, 2000b; Dojlido *et al.*, 1999). The addition of ozone (O_3), a gas produced primarily by subjecting oxygen molecules to high electrical voltages is an alternative and efficient disinfection reagent (Twort *et al.*, 2000b). Disinfection by chlorine dioxide gas is also a potent disinfection process that is an alternative to chlorine gas. UV irradiation is another effective process that uses electromagnetic radiation in wavelength between 100 and 400 nm (ultraviolet spectrum) for water disinfection (USEPA, 2003b).

A trade-off of the benefits and disadvantages of each of the disinfection methods and their respective significant DBPs formed are summarised in Appendix 1. No one process provides a complete solution. Disinfection by chlorine gas is by far the most applied disinfection process owing to its effectiveness, well studied consequences and relatively low cost of implementation.

1.7.5.3 Influence of chlorine dose

The concentration of the disinfectant used has a strong influence on the formation of THMs and HAAs. An increase in the chlorine dose correlates with an increase in the formation of THMs and HAAs, until the reaction is no longer chlorine limiting (Carlson *et al.*, 1998; El-Shafy *et al.*, 2000; Nikolaou *et al.*, 2004a). Nikolaou *et al.*, (2004) reported that the chorine dose was one of the most important factors for DBP formation, as an increase in chlorine dose from 3 mg/l to 30 mg/l had a 6-fold increase in chloroform formation, at 3 °C.

The decay in chlorine concentration is initially rapid after introduction into water and slows down after some time period has elapsed. There are two mechanisms for the decay of chlorine after introduction to water, one is rapid (oxidation of inorganic compounds) while the second is notably slower (reactions with NOM) (Boccelli *et al.*, 2003). The reaction rates of chlorine are dependent on several factors, such as source water characteristics , contact time in the treatment plant and distribution system, and the characteristics of the distribution system (such as pipe age and pipe material) (Boccelli *et al.*, 2003).

1.7.5.4 The control of HAAs and THMs

There are various methods for the control of DBPs reported in the literature, which include:

- Reducing amount of natural organic matter present, by using processes that remove these compounds during treatment (Chow *et al.*, 2009);
- Modifying the disinfection process *e.g.* using chloramination rather than chlorination can reduce the concentration of THMs and HAAs (Kawamura, 2000);
- Optimising the disinfection conditions by reducing the parameters that influence its formation (Kim, 2009).
- Improving source water protection by preventing the introduction of pesticide contamination or wastewater effluents which could be a source of the DBP precursors.

If DBPs enter the potable water supply, then at source remedies can be used to remove the volatile THMs such as boiling, refrigeration and filtering. HAAs, however, are not volatile hence cannot be removed by boiling or refrigeration, but can be removed by filtration (Levesque *et al.*, 2006).

1.8 Analyses of water pollutants

This research focuses on the analyses of DBPs, primarily THMs and HAAs, using gas chromatography based methods. THMs and HAAs have different physical and chemical parameters and hence require different sample introduction and analysis techniques.

1.8.1 Gas chromatography (GC)

Gas chromatography is a well established analytical technique. The principle of chromatographic separation is that when a mixture of compounds is passed along a medium (stationary phase) by another medium, (mobile phase), the various species of compounds will move at different rates to one another, and therefore, become separated. In gas chromatography, the mobile phase is typically one of the inert gases helium, hydrogen or nitrogen and a high temperature enables the separation of volatile compounds Figure 1.2 shows a schematic of a gas chromatograph.

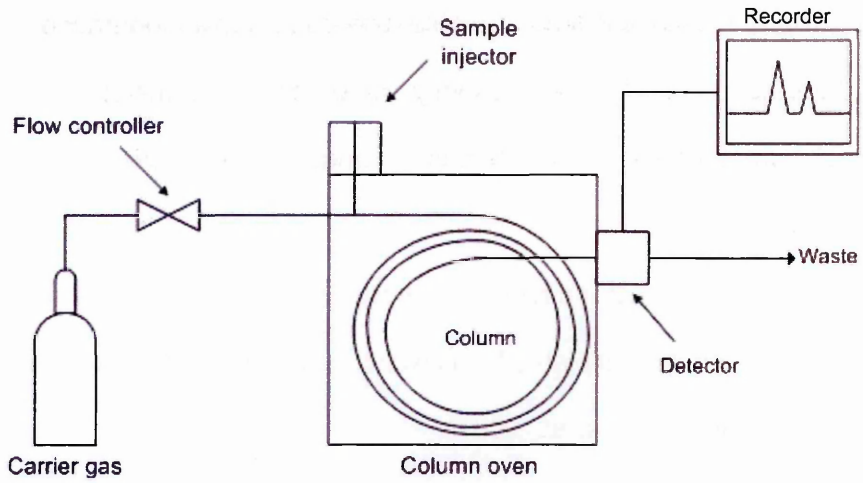


Figure 1.2: A schematic drawing of a gas chromatography system.

The concept of gas chromatography (or gas-liquid chromatography) was first discussed in 1941 by Martin and Synge during the development of liquid-liquid chromatography (Martin *et al.*, 1941). However, it was not until 1952, that this idea was demonstrated experimentally by James and Martin, through the separation of fatty acids using an automatic acid-base titration detector (James *et al.*, 1952).

The practical application of gas chromatography relies on the use of suitable detectors. The development of GC detectors started with the invention, by Ray, of the katharometer detector or thermal conductivity detector (Ray, 1954). This led to the development of several other detectors such as the gas density meter by Martin and James (Martin *et al.*, 1956), the flame ionisation detector by J. Harley *et al.* and McWilliam and Dewar (Harley *et al.*, 1958; McWilliam *et al.*, 1958), and the invention of the electron capture detector by James Lovelock (Lovelock, 1958). Also in the late 1950s, Gohlke and McLafferty developed the powerful combination of chromatography with mass spectrometry (Gohlke *et al.*, 1959).

The earliest columns were composed of packed tubes, referred to as 'packed columns', and used activated silicone oil or charcoal as the stationary phase. However, following the development of narrower capillary columns, pioneered by Marcel Golay, the use of packed columns began to decline owing to the superior performance of the newer design

(Golay, 1958; Golay *et al.*, 1958). Capillary columns enable higher-resolution separations with shorter run times and greater peak capacity. Presently, hundreds of designs of capillary columns are in widespread use, usually with lengths ranging between 10 - 60 m, and inner diameters of 0.20 - 0.53 mm. They generally consist of a fused silica tube with an external polyimide resin which can withstand high temperatures (< 370 °C). Column efficiency is often expressed on a theoretical plates basis which can be related to the ratio of the retention times and peak width (Barry *et al.*, 2007).

GC based systems require compounds to be thermally stable and volatile. To enable GC separation of non-volatile compounds it is common to make the compounds more volatile, for example through derivatisation (Domino *et al.*, 2004). As a consequence, it has been estimated that 10 - 20 % of known compounds can be analysed by gas chromatography (Agilent, 2007a). Modern day GC systems range in cost, complexity and precision. High performance systems are used for research and development; robust GC systems are used for large-scale routine analyses, while some GC systems are specifically developed for fast, rugged and portable solutions for real-time measurements (Agilent, 2007a).

1.8.1.1 The electron capture detector (ECD)

The ECD is highly sensitive to molecules containing highly electron-capturing and electronegative functional groups such as halogens, peroxides, quinones, and nitro-groups. Halogens have a response that is 100 - 100,000 times greater than that obtained for hydrocarbons. Similarly, the response for nitrates is 100 - 1000 times greater. Carbonyls have 20 - 100 times better responses than hydrocarbons (Colon *et al.*, 2004). Detection limits of < 100 femtograms have been reported for the analyses of halogenated hydrocarbons (Göran *et al.*, 1978). This type of detector has therefore been widely used for the analyses of both THMs and HAAs (USEPA, 1979b; USEPA, 1990; USEPA, 1992; USEPA, 1995b; USEPA, 1998a; USEPA, 2003a).

The design of an ECD consists of a cell plated with a radioactive isotope ^{63}Ni. The ^{63}Ni releases ß particles that collide with the make-up gas molecules to produce low energy electrons Electrons produced by a filament are of higher energy hence unsuitable for this purpose. The detector can function in two ways: either a constant DC potential is applied across the detector or a pulsed potential is used (Zlatkis *et al.*, 1981). The free electrons produce a small current called the 'reference' or 'standing current'. When the column eluents are exposed to the free electrons, compounds with the highest electron affinity (such as halogens) preferentially capture the electrons and reduce the current in the cell. The reduction in current is measured by an electrometer (Jinno, 2004). The response of the electron capture depends upon many variables such as the chemical composition of the analyte, its concentration, the cleanliness of the cell, the inlet, the column and instrument settings such as detector temperature, make-up flow-rates, and reference current (Agilent, 2007b). The electron capture detector is one of the most popular GC detectors in use today, and has revolutionised environmental analyses, in particular low-level pesticide detection (Scott, 2004). One drawback of using an ECD, particularly beyond a standard analytical laboratory, is the legislative requirement of having a permit for the radioactive ^{63}Ni source present (Agilent, 2007a; HSE, 1999).

1.8.1.2 Mass spectrometry (MS)

Mass spectrometry enables the separation of molecules of different relative molecular or isotopic mass. The history of mass spectrometry began with Joseph Thomson, whose studies on electrical discharges in gases led to the discovery of the electron in 1897 (Thomson, 1897). This work contributed towards the construction of the first mass spectrometer (then called a parabola spectrograph) for the determination of mass-to-charge ratios of ions in 1913 (Thomson, 1913). In 1919, Francis Aston designed a higher resolution mass spectrometer allowing him to study isotopes (Aston, 1919). During the same period, Arthur Dempster developed a higher resolution magnetic mass analyser (Dempster, 1918).

However, two of the major developments in mass spectrometry occurred with the design of the time-of-flight and quadrupole mass analysers. Time-of-flight mass spectrometry (ToFMS) was first described by William Stephens and is based upon the concept that ions of different mass to charge ratios take different times to traverse a given distance (Stephens, 1946). However, it was not until 1955, that Wiley and McLaren produced the first commercial ToF mass spectrometers (Wiley *et al.*, 1955). At the same time advances in the quadrupole and quadrupole ion trap mass spectrometers were made by Paul Wolfgang (Wolfgang *et al.*, 1953). Parallel research by Johnson and Nier resulted in the development of a high-mass-resolution double-focusing instrument to perform isotopic analysis and separation (Johnson *et al.*, 1953).

The direct coupling of GC and ToFMS was achieved by Gohlke and McLafferty (Gohlke *et al.*, 1959). The union of gas chromatography with mass spectrometry is an extremely powerful combination. Santos and colleagues, described GC-MS as an 'advantageous and powerful technique because of its good sensitivity, versatility and selectivity as compared to other detection systems' (Santos *et al.*, 2003). The GC-MS is a universal analytical detector, a 'gold standard' for trace analysis in most standard analytical laboratories. It has been extensively used in the fields of forensic chemistry, pollution chemistry, environmental & water studies, pharmaceutical chemistry and toxicology.

An overview of the three basic components of mass spectrometers; namely the ionisation source, the mass analyser and the ion detector is summarised below:

The ionisation source: The mass spectrometer may be fitted with one of a number of different ionising sources, such as: electron impact (EI), chemical ionisation (CI), atmospheric pressure ionisation (API), inductively coupled plasma ionisation (ICP), electro spray ionisation (ESI), fast-atom bombardment (FAB), field ionisation, laser ionisation (LIMS), matrix-assisted laser desorption ionisation (MALDI), plasma-desorption ionisation

etc (Hoffmann *et al.*, 2007). However, the two most common ionisation sources utilised in commercial systems, and the two most relevant to this thesis, are EI and CI:

Electron impact ionisation (EI): Authur Dempster developed the first electron impact source in 1921 (Dempster, 1921). It is still widely used in modern mass spectrometers. EI is a so called 'hard' ionisation technique, where the sample molecules are directly bombarded by a stream of high-energy electrons. The sample molecules are ionised to radical cations. The excess energy causes extensive fragmentation of the molecules forming a pattern, which is unique to the specific compound. An ionisation energy of 70 eV is widely accepted as the standard setting for mass spectral studies. Extensive spectral library databases containing over 562,000 spectra, such as the NIST and Wiley libraries, are available for organic compounds generated on a variety of instruments at 70 eV (Website - Sisweb, 2011).

Chemical ionisation (CI): Munson and Field developed the first CI source in 1966 (Munson *et al.*, 1966). CI is a 'soft' ionisation technique that introduces a reagent gas to the ion sources at pressures of 13 - 300 Pa. Usually, the molecular structures of the sample molecules are maintained because less energy is transferred to the samples resulting in lower fragmentation. Common reagent gases include methane, isobutane and ammonia (Harrison, 1992). The chemical ionisation process produces both positive (cations) and negative ions (anions) and thus either positive-ion chemical ionisation (PCI) and negative-ion chemical ionisation (NCI) is available. In chemical ionisation, there are four general ionisation pathways that form ions from neutral sample analytes and reagent gas. These are proton transfer, electrophilic addition, anion abstraction and charge exchange (Gross, 2004).

As the DBPs contain halogens, the most relevant technique is NCI, where the electrons emitted by the filament, at 70 eV, are 'thermalised' by a cloud of the reagent gas ions, *i.e.*

lose some of their excess energy. The low-energy electrons can have a very narrow distribution ranging from 0 to ~ 5 eV (Masucci *et al.*, 2004). Under pressure, the electrons react with sample molecules to produce radical anions. These anions are selectively captured by molecules with high electron affinity such as polyaromatics, halogens and nitro groups. NCI has been reported to be up to 10 - 100 times more sensitive than PCI (Masucci *et al.*, 2004). NCI involves an ion/molecule reaction either to add an anion to a gas-phase analyte molecule or to abstract a proton from the analyte molecule. In addition, under the same conditions as NCI, electron capture negative ionisation (ECNI) is also possible (Watson *et al.*, 2008). ECNI does not involve an ion/molecule reaction, instead it involves the direct interaction of the analyte molecule with a thermal electron (0 - 15 eV) generating negative ions. This is most likely to take place by dissociative electron capture, as shown in Equation 1.4 (Watson *et al.*, 2008)

$$AB + e^- (0 - 15\ eV) \rightarrow A + B^- \qquad \text{Equation 1.4}$$

It may also be possible that ion pair formation is also taking place, as shown in Equation 1.5 (Watson *et al.*, 2008)

$$AB + e^- (> 10\ eV) \rightarrow A^+ + B^- + e^- \qquad \text{Equation 1.5}$$

In PCI, the most common ionisation pathway is proton transfer, where sample molecules are ionised to cations with the level of excess energy deposited in these cations depending on the thermochemistry molecule reaction (Harrison, 1992).

The mass analyser: The main function of the mass analyser is to separate, or resolve, the ions formed in the ionisation source of the mass spectrometer according to their mass-to-charge (*m/z*) ratios. There are a number of mass analysers currently available including quadrupoles, time-of-flight (ToF), magnetic sectors, linear ion traps and quadrupole ion traps.

The quadrupole (also called quadrupole mass filter) is a scanning instrument, which consists of four parallel poles or rods. It separates ions by the simultaneous application of a direct current (DC) and radio frequency fields (RF). Scanning is accomplished by systematically changing the field strengths, thereby changing the *m/z* value that is transmitted through the linear analyser. The design of quadrupole mass spectrometers enables an easy interface to various inlet systems, they are also typically cheaper than other designs (Siuzdak, 2006). Quadrupole mass spectrometers (Agilent 5973 and 5975) are utilised for the analysis of HAAs in this thesis.

The ion trap analyser is another scanning instrument separating ions by simultaneously changing a DC and RFs. The quadrupole ion trap consists of one ring electrode and two end cap electrodes, while the linear ion trap consists of four parallel poles confined by two end cap electrodes. The motion of the ions induced by the electric field on these electrodes allows ions to be trapped or ejected from the ion trap. A quadrupole ion trap analyser (Varian Saturn 2000) was used for the analysis of the concentrations of THMs.

The ToF analyser is non-scanning, in that, the ions are separated by differences in their velocities because of their differing mass-to-charge ratios and not through the modification of electric fields. The application of a constant amount of kinetic energy to a mixture of ions causes the lighter ions (smaller *m/z*) to move faster along a flight tube than the heavier ions. All ions hitting the detector are recorded simultaneously. Modern ToFs have been coupled with an electrostatic mirror or reflectron. The electrostatic mirror placed at the end of the first flight tube reflects the ions onto another second flight tube, thus increasing the path length. This enables ToF reflectron to provide a higher *m/z* resolution, compared to quadrupole and ion trap (Siuzdak, 2006).

The ion detector: Once the mass analyser separates the ions, they reach the detector, which generates a current signal from the incident ions. Some of the common detectors are the photomultiplier, the electron multiplier, the faraday cup and the micro-channel

plate. The electron multiplier is one of the most commonly used ion detectors (Dass, 2007). It generates a measurable current from the cascade of electrons resulting from the impact of incident ions hitting the detectors surface (consisting of a series of aluminium oxide (Al_2O_3) dynodes).

1.8.1.3 Comprehensive two-dimensional gas chromatography (GC×GC)

Standard GC analysis, conventionally termed as one-dimensional gas chromatography (1D GC), uses a single chromatographic column, as previously shown in Figure 1.2. Comprehensive, or two-dimensional, gas chromatography (GC×GC) is accomplished by the serial coupling of two GC columns (of different polarity) using a modulator as an interface; the systems detector records the signal at the end of the second column. The thermal modulator is responsible for continuously trapping and re-focusing of compounds so that the constant elution from the first column can then be injected into the second column in discrete fractions. This allows the separation of compounds across two dimensions because of the differing polarity of the two columns. Comprehensive chromatography therefore allows the possible resolution of compounds that were previously hidden by a dominant co-eluting species within a one dimensional GC study. The first demonstration of GC×GC was by Liu and Philips, in 1991, when they analysed coal liquids (Liu *et al.*, 1991). A schematic of a GC×GC system is given in Figure 1.3.

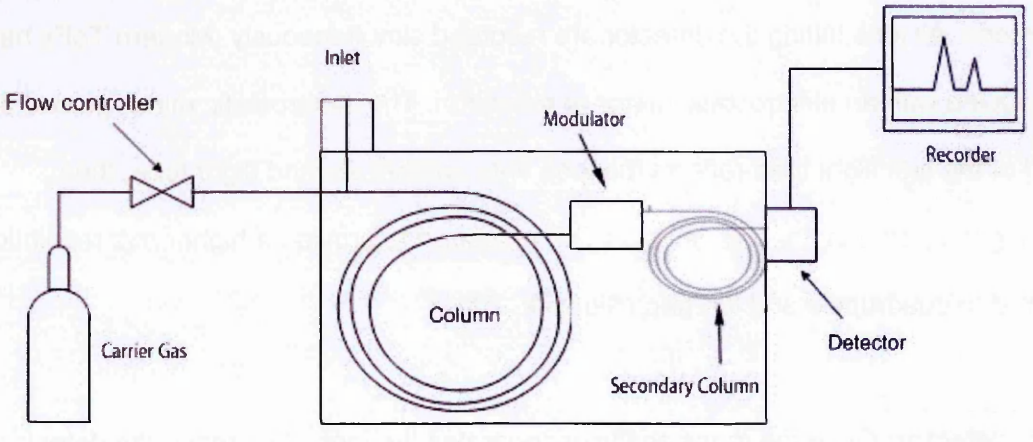


Figure 1.3: A schematic of a comprehensive two-dimensional gas chromatography (GC×GC) system.

Comprehensive chromatography with its independent but combined non-polar and polar separations, can resolve many compounds and has significantly greater peak capacity, compared to 1D GC (Górecki *et al.*, ; Panic *et al.*, 2006). The cycle of re-focusing and re-injection is matched to the time required for compounds to elute from the second GC column, resulting in a separation of compounds across a plane, rather than just along a line, creating a two-dimensional chromatogram. For the orthogonality criteria to be satisfied, the separations must be based on different separation mechanisms such as polarity and volatility. GC×GC has been used for the determination of target and unknown compounds within complex mixtures of petroleum, pesticides, oil, fragrances, and cosmetics (Focant *et al.*, 2004; Marriott *et al.*, 2003; Panic *et al.*, 2006; Shellie, 2009; Silva Jr *et al.*, 2009). No publication has yet reported the use of GC×GC for the analysis of HAAs.

The technology of GC×GC has been further enhanced by coupling of a comprehensive GC×GC to a highly sensitive mass spectrometer to improve peak capacity and compound resolution. Specifically, the use of a time-of-flight mass spectrometer (ToFMS) as a detector allows an acquisition of up to 500 mass spectra/s and the accurate profiling of each GC×GC peak. Additionally, the absence of concentration skewing in the ToFMS instrument ensures spectral continuity and allows mass spectral deconvolution of co-eluting chromatographic peaks characterised by different fragmentation patterns. The use of specialist software (deconvoluted ion current (DIC) algorithm) and ToFMS has resulted in a powerful instrument combining the improved chromatographic resolution of a GC×GC and the analytical resolving power of a ToFMS. Owing to the use of two chromatographic columns, a mass spectrometer and DIC algorithm, the GC×GC-ToFMS is marketed as a system that separates compounds in four dimensions. The disadvantages of the instrument are that it is more expensive, has higher running costs, and requires longer data processing time. A Leco Pegasus IV fitted with a thermal modulator was used for the detection of HAAs in Chapters 5 and 6.

1.8.1.4 Sample introduction and enrichment techniques

The preparation of samples so that they are amenable to gas chromatography (e.g. converting non-volatile compounds to volatile ones) is an important consideration, particularly for the analysis of trace contaminants. Some of the introduction and enrichment techniques, which have been used for the analyses of THMs and HAAs, are summarised below:

Liquid: This is the most common injection method where the compounds of interest are extracted into a liquid solvent and injected using a microsyringe into the GC inlet in the liquid phase. This method has been used for the analyses of THMs and derivatised HAAs (USEPA, 1995b).

Purge and Trap (PT): In PT, volatile components suspended in a liquid solution are forced out by the purging of a stream of inert gas, allowing their subsequent trapping onto an adsorbent. The trapped volatiles are then thermally desorbed or eluted with a suitable solvent. Purge and trap has been widely reported for the analyses of THMs (USEPA, 1979a; USEPA, 1995c).

Headspace: This involves the analysis of the equilibrated vapour above a sample in a vial utilising the distribution of the volatile analytes in the gas phase. Headspace techniques can be classified into static and dynamic (Biziuk *et al.*, 1996). Static headspace is the simplest technique, as it involves the injection of an aliquot of the gaseous phase which is in thermodynamic equilibrium with the liquid sample at a set temperature. The equilibrium is governed by parameters such as the temperature of the sample, volume of the sample, syringe temperature, sample mixing, equilibrium time and the addition of any matrix modifier (Kolb *et al.*, 1997; Turner, 2007). This technique has been used for the analyses of the volatile THMs (Nikolaou *et al.*, 2002b; Takahashi *et al.*, 2003). Dynamic headspace is the trapping of the headspace equilibrated above the sample with an absorbent trap. The sample can then be thermally desorbed onto the GC or eluted with a solvent.

Dynamic headspace uses both mobile gas and liquid phases for its separations. This technique has also been used for the analyses of THMs (Wang *et al.*, 1995).

Solid phase micro extraction (SPME): Developed by Arthur and Pawlisyzn in 1990, SPME is a sample preparation technique that uses a needle containing a fused silica fibre coated with an appropriate stationary phase (Arthur *et al.*, 1990). The sample preparation can be carried out by direct immersion of the fibre into the sample or *via* the exposure of the fibre to the headspace above liquid or solid sample (HS-SPME). The fibre is then thermally desorbed at the GC inlet eluting the compounds of interest. The benefit of SPME is good sensitivity with faster and robust analyses, compared to headspace analyses. To tailor the technique for a particular application, different stationary phases, such as carboxen-polydimethylsiloxane (CAR/PDMS), carbopack-Z and polyethylene glycol (PEG), are commercially available. Analysis of THMs and derivatised HAAs using SPME as the sampling technique have been previously reported by Stack and colleagues (Sarrión *et al.*, 1999; Stack *et al.*, 2000).

1.8.2 Common analytical methods reported for the analysis of THMs

THMs are volatile compounds and hence can be easily analysed by gas chromatographic techniques using detectors such as ECD and MS. The USEPA have established several alternative methods for the measurement of THMs. USEPA Methods 501.1, 501.3 and 524.2 utilise purge and trap-gas chromatography coupled to a mass spectrometer (PT-GC-MS) for the analyses of THMs in drinking water (USEPA, 1979a; USEPA, 1995c; USEPA, 1996b). USEPA method 502.2 uses purge and trap-gas chromatography with a photoionisation detector connected in series to an electrolytic conductivity detector (PT-GC-PID-ELCD)(USEPA, 1995a). The purge and trap method is one of the popular methods used for the analyses of THMs, because they provide good accuracy, precision and lower detection limits (compared to other methods such as headspace) (Emmert *et al.*, 2004; Lara-Gonzalo *et al.*, 2008). The purge and trap methods work well with lower sampling schedules, where samples are taken monthly or quarterly. However, when

sampling rates are higher, this method has been reported as being cumbersome (Emmert *et al.*, 2004).

USEPA Methods 501.2, 551 and 551.1 all use liquid-liquid extraction of the water sample followed by GC analysis equipped with an electron capture detector (LLE-GC-ECD). Other non EPA methods for analysing THMs though LLE and PT are also found in literature (Culea *et al.*, 2006). These include analysis by dry electrolytic conductivity detector (PT-GC-DELCD) (Brown *et al.*, 2007).

Many of the other published methods for the THM analyses focus on developing or improving sample extraction or sample introduction onto the GC. These methods include static HS (Caro *et al.*, 2007; Culea *et al.*, 2006; Golfinopoulos *et al.*, 2001; Kuivinen *et al.*, 1999; Nikolaou *et al.*, 2002b; Toussaint *et al.*, 2001); Dynamic HS (Wang *et al.*, 1995); HS-SPME (Stack *et al.*, 2000); Solid phase extraction (SPE) (Nobukawa *et al.*, 2001); HS-liquid phase micro extraction (Zhao *et al.*, 2004); Capillary membrane sampling (CMS) (Brown *et al.*, 2006); and direct aqueous injection (DAI) (Golfinopoulos *et al.*, 2001),

Besides conventional GC techniques other techniques such as membrane introduction mass spectrometry (MIMS) and capillary membrane sampling-flow injection analysis method with nicotinamide fluorescence (CMS-FIA NCA-FL) have also been reported (Bauer *et al.*, 1994; Chang *et al.*, 2000c; Geme *et al.*, 2005; Lopez-Avila *et al.*, 1999).

A comprehensive overview of the performance of common THM analytical methods reported in the literature is provided in Appendix 1.

Some of the common problems associated with the use of these methods are:

- Liquid-liquid extraction requires the use and disposal of several solvents and time-consuming sample preparation;

- Purge and trap analyses can be easily affected by interfering compounds which can lead to problems such as poor recoveries, aberrant peak shapes and the disappearance of individual analytes from the chromatogram (Supelco, 1997). For the analyses of water samples, the trap can be deactivated by foam produced in the water and can introduce thermal decomposition products from non-volatile compounds (Lee *et al.*, 1997). When sampling rates are higher, this method has been reported as being cumbersome (Emmert *et al.*, 2004);
- Headspace analysis is the simplest method but has the lowest analytical sensitivity. It is, however, reported to overestimate THMs in certain water samples (Cammann *et al.*, 1993; Takahashi *et al.*, 2003);
- Solid phase micro extraction can be affected by interfering compounds, contamination with metallic particles originating from the SPME unit itself, and can lead to inadequate repeatability (Haberhauer-Troyer *et al.*, 2000; Verhoeven *et al.*, 1997).

As part of the development and optimisation process, all but PT of the above methods were further investigated and optimised, as described in Chapter 4, for the robust and rapid measurement of THMs. The methods investigated further were HS-GC-MS, HS-SPME-GC-MS, HS-GC-μECD and LLE-GC-μECD.

1.8.3 Common analytical methods reported for the analysis of HAAs

HAAs are non-volatile compounds that need to be extracted, concentrated and derivatised prior to their analysis in a GC-based system. There are several methods reported in literature for the analysis of HAAs in water. USEPA Methods 552.1, 552.2 and 552.3 use liquid-liquid micro extraction (LLME) coupled with bench-top GC-ECD (USEPA, 1992; USEPA, 1995b; USEPA, 2003a). The advantages of using LLME for HAA analyses are its good selectivity, low detection limits and a wide linear range. However, the disadvantages include the need for sample pre-treatment, which is time consuming and labour intensive and therefore, subject to multiple procedural errors. Non EPA methods using liquid

extraction have also been reported (Nikolaou *et al.*, 2002a). Alternative derivatisation strategies using GC-ECD or MS, such as difluoroanilide derivatisation, acidic ethanol derivatisation, *in-situ* anilide derivatisation have also been reported (Ozawa, 1993; Scott *et al.*, 1998).

The concentration of HAAs present in water samples has also been analysed by GC-MS in EI mode (Williams *et al.*, 1997; Xie, 2001). NCI mode has also been used for the analyses of HAAs in biological samples (Jia *et al.*, 2003). HS-SPME-GC-MS has been used for comparison of US EPA method derivatisation and acidic ethanol derivatisation (Sarrión *et al.*, 2000). Solid phase extraction coupled with a GC-μECD analyses of HAAs in drinking water has also been reported (Pervova *et al.*, 2002).

Several non-GC separation methods have been investigated for the determination of HAAs. These include ion chromatography-mass spectrometry (IC-MS) (Liu *et al.*, 2004), ion chromatography-tandem mass spectrometry (IC-MS-MS) (Harman *et al.*, 2011), high pressure liquid chromatography-electrochemical detection (HPLC-EC) (Carrero *et al.*, 1999), solid-phase extraction-capillary electrophoresis (CE) with UV detection (Martínez *et al.*, 1999), (high-field asymmetric waveform ion mobility spectrometry-electrospray ionisation-mass spectrometry (FAIMS-ESI-MS) (Ells *et al.*, 2000), capillary electrophoresis-electrospray ionisation - mass spectrometry CE ESI-MS (Urbansky, 2000), ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS) (Liu *et al.*, 2004), solid-phase extraction-liquid chromatography electrospray ionisation mass spectrometric detection (SPE-LC-ESI-MS) (Takino *et al.*, 2000) and solid phase extraction-ion chromatography (SPE-IC) (Barron *et al.*, 2004). A comprehensive overview of the HAAs methods reported in literature have been summarised in Appendix 1.

At the start of this study, only Malliarou *et al.* (2005) had analysed HAA concentrations in UK water samples. They used a GC-μECD for the analysis. In collaboration with Cranfield Water Science Institute, this thesis explores the development and optimisation of

alternative mass spectrometer based methods for the analyses of HAAs (Chapter 5). Specifically GC-MS (EI), GC×GC-ToFMS and GC-MS (NCI) were explored and evaluated against the analytical performance (in terms of their linearity, repeatability, accuracy and limits of detection) from an optimised method for use on a GC-μECD.

1.9 Early monitoring of potable water systems

For monitoring THMs, accurate, precise, and sensitive analytical methods are needed directly in the drinking water distribution system (Emmert *et al.*, 2004). The development of such measurement methods for on-line monitoring should improve the management of THM concentrations in treatment plants and drinking water distribution systems

Gullick *et al.* have suggested the following key criteria for the design of an early water monitoring system (Gullick *et al.*, 2003):

- Provides warning in sufficient time for action
- Requires low skill and training
- Affordable cost
- Is sensitive to quality changes at regulatory levels
- Gives minimal false positive or negative responses
- Is robust, reproducible and verifiable
- Allows remote operation and functions all year-round

They also suggested a list of factors that should be considered when selecting a specific method for a monitoring system, which included, method response sensitivity, speed, desired frequency of analyses, means of data development and retrieval, maintenance and labour requirements, initial and ongoing costs, and space availability.

1.10 Thesis Objectives

As reported earlier, the overall aim of this project was to develop, optimise and evaluate new and existing analytical protocols for the analysis of THMs and HAAs from UK water sources. This thesis will:

- Provide a detailed analysis of the temporal variance of THM and THM4 concentrations, and parameters relevant to their formation, as obtained from selected sites in the potable water distribution system of Yorkshire Water Services Ltd from 1998 - 2007;
- Evaluate existing analytical methods for the analysis of THMs and report on the development and optimisation of selected methods (HS-GC-MS, HS-SPME-GC-MS and HS-GC-μECD). Their performance, in terms of their linearity, repeatability, accuracy and detection limits, will be reported along with their viability for near-real time monitoring.
- Investigate the suitability of several gas chromatographic methods (GC-μECD, GC-MS (in electron impact ionisation and chemical ionisation modes) and GC×GC-ToFMS) for the analysis of HAAs present in water samples. The parameters for HAA analysis by GC-μECD will be optimised and evaluated in terms of its linearity, repeatability, accuracy and LOD against published methods.
- Determine and report the influence of various disinfection parameters (contact time, pH, bromide ion concentration and water temperature) on the formation of THMs and HAAs, under controlled laboratory conditions, during chlorination of treated water from lowland and upland sources in the UK. Evaluate the suitability of the optimised methods developed (GC-μECD and GC×GC-ToFMS) for the measurement of HAA concentrations in treated water samples. Evaluate if THM concentrations could be used as a surrogate for HAA concentrations in the UK waters.
- Determine and report the influence of various disinfection parameters (contact time, pH, bromide ion concentration and water temperature) on the formation of THMs and

HAAs, under controlled laboratory conditions, during chlorination of treated water from lowland and upland sources in the UK. Evaluate the suitability of the optimised methods developed (GC-μECD and GC×GC-ToFMS) for the measurement of HAA concentrations in treated water samples. Evaluate if THM concentrations could be used as a surrogate for HAA concentrations in the two specific UK waters.

- Determine the concentrations of each of the nine halogenated HAAs, the total concentration of the nine HAAs (HAA9) and the US regulated HAA5, from thirteen sites within five water utility companies, across England using the optimised analytical method developed. Prior to the commencement of this research studentship, only one published study had reported measurements for HAA concentrations in UK potable water sources.

2. An analysis of the temporal variations in THM concentrations and other parameters relevant to the formation of disinfection by-products in the drinking water distribution system of Yorkshire Water Services Ltd

2.1 Introduction

Yorkshire Water Services Ltd (YWS) regularly monitors its water systems to ensure it provides the highest quality water for its customers and to comply with its legislative obligations set by the England and Wales's Drinking Water Inspectorate (DWI). Several parameters such as pH, temperature, total THM (THM4) concentration, pesticides, coliforms, *etc.* are regularly measured across its water distribution systems (A complete list of the parameters measured has been summarised in Appendix 1).

The Water Supply Regulations 2010 has set the maximum threshold value for the total concentration of THMs at 100 µg/l, in a single sample, at the customer tap (DWI, 2010c). These levels maintained those previously specified in The Water Supply (Water Quality) Regulations 2000 (England) (DWI, 2000). Prior to this, the water companies had to keep their THM4 concentrations below 100 µg/l on a 3-month rolling average. In areas where fewer than four samples were taken in any year no sample should have exceeded 100 µg/l (DWI, 1989).

Each company's region has been split into water supply zones, which are limited to a maximum population of 100,000. These water supply zones were established for regulatory monitoring and reporting purposes. The frequency of sampling depends on the population of the supply zone and volume of the treatment works, with an annual

maximum of 48 samples taken (DWI, 2010b). Sampling at service reservoirs has been set at one sample a week, when a reservoir is in use. YWS's distribution system is located in the Northern region of England, as categorised by the DWI and shown in Figure 2.1. YWS is the second largest water supplier in the Northern region (1.2 billion litres to 4.7 million customers), after United Utilities Water (1.8 billion litres a day to 6.8 million customers).

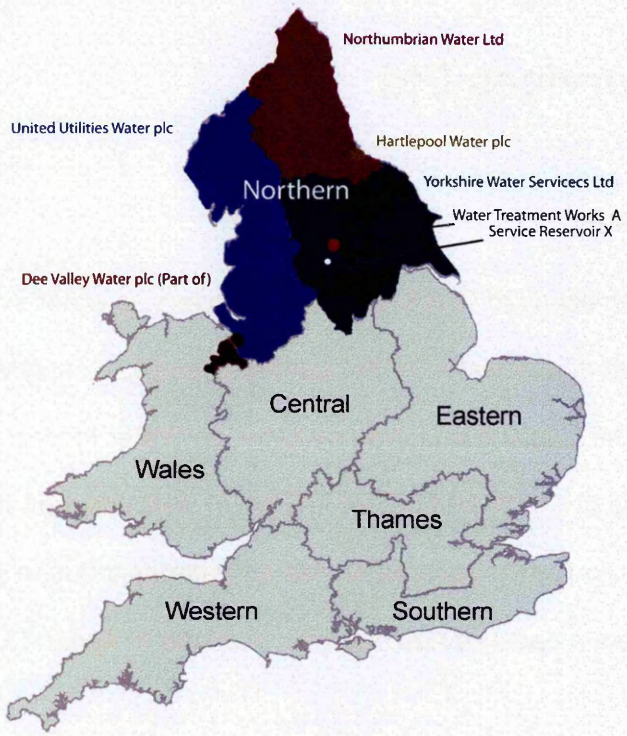


Figure 2.1: A map showing Wales and the six regions of England as specified by the DWI. Yorkshire Water Services and other water companies in the Northern Region of England are shown. The approximate locations of the Water Treatment Work A and Service Reservoir X are also shown. The service reservoirs are located in the YWS distribution system (Green area) (Diagram obtained from DWI, 2009).

This chapter aims to provide an overview and analysis of the levels of THM4 concentration, pH, temperature and residual chlorine measured across Yorkshire Water Service's main drinking water distribution system in order to contextualise the studies in this thesis.

As an initial investigation, data on the individual and THM4 concentrations from twenty five service reservoirs, across their distribution network, were made available for the period between June 2006 - June 2007. Data for other parameters that influence the formation of THMs such as NOM, bromide concentrations, and chlorine dose were not available.

A more detailed study used data from a Water Treatment Works (assigned as A) and one of its service reservoirs (assigned as X). Data for total THM4 concentrations were available for most of the sampling period between January 1998 - June 2007 (with a few short periods of no data); pH and residual chlorine was available for most of the period between January 1998 - June 2006; while temperature and individual THM4 data were only available at irregular periods within the sampling range.

The THM analyses were performed for YWS by an external analytical company using the established USEPA Method 551.2 (PT-GC-MS). No additional details were made available on the analytical parameters used. The methods used to measure pH, temperature, and residual chlorine were also not disclosed. However, it was believed that Standard Methods for the Examination of Water and Wastewater were used (Eaton *et al.* 2005). The raw data were kindly provided by Yorkshire Water Services Ltd.

2.2 THM4 concentrations across 25 sites in Yorkshire Water's distribution system (June 2006 - June 2007)

The sampling rate at these sites ranged from 2 - 5 times a month (n=20 to 55). The THM4 concentrations were plotted across the sites, as shown in Figure 2.2.

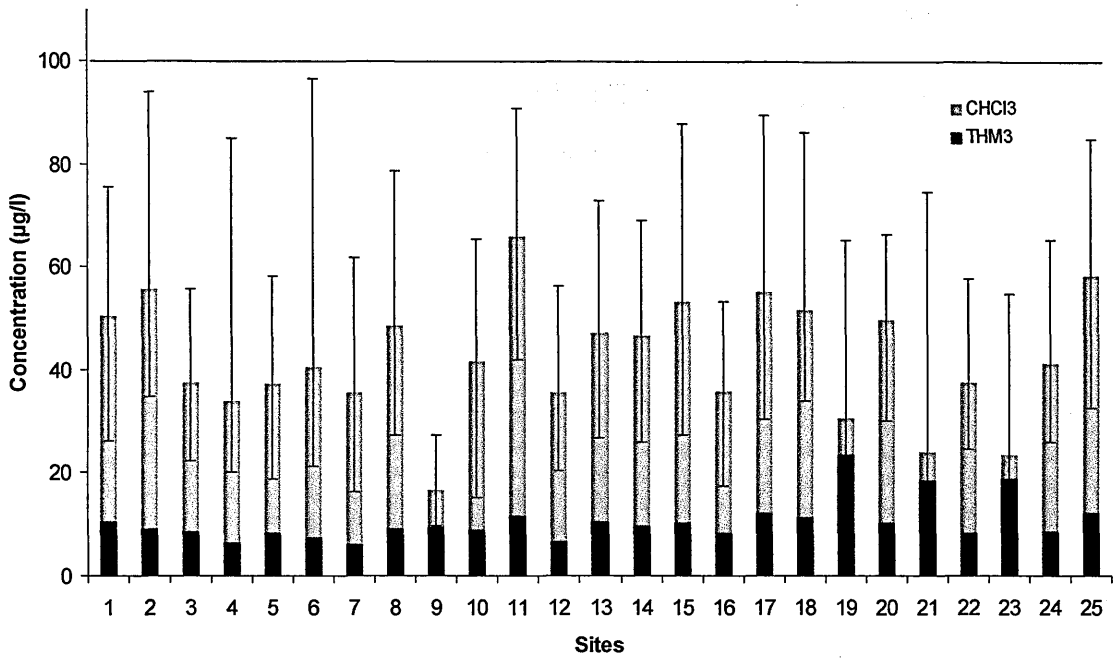


Figure 2.2:The concentrations of THM4 for the period June 2006 - June 2007 across 25 different sites within Yorkshire Water Service's distribution system. The bars represent the mean THM4 at each site. The lighter shade of each bar shows the proportion of $CHCl_3$ while the darker shade represents the sum of the other three THMs (i.e. $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$). The whiskers represent the maximum and minimum THM4 at each site during the period (and not the σ_{n-1}).

The lowest mean concentration across the 25 sites during the period was 16.6 µg/l (at Site 9) and the highest was 65.9 µg/l (at Site 11). The highest THM4 levels was found at Site 6 (96.6 µg/l) in August 2006, while the lowest THM4 concentration was found at Site 19 (6.5 µg/l) in December 2006. Site 6 showed the greatest difference between the individual maximum and minimum concentrations at 75 µg/l.

$CHCl_3$ was the most abundant THM in the service reservoirs. With the exception of four sites, the proportion of $CHCl_3$ across the other 21 sites averaged 78.8 % (75.0 - 82.4%). The four sites, 9, 19, 21 and 23, had relatively low $CHCl_3$ abundances at 42.0, 17.8, 13.5 and 12.7 %, respectively. In addition, the mean THM4 concentrations at these sites, were also relatively low at 16.6 - 30.6 µg/l. Whereas, the mean THM4 level at the other 21 sites ranged from 33.9 - 65.9 µg/l. $CHCl_2Br$ was the second most abundant THM (mean concentration of 7.6 µg/l) present in most of the service reservoirs, followed by $CHClBr_2$ (mean 2.9 µg/l) and $CHBr_3$ (mean 1.1 µg/l).

2.3 Water Treatment Works A

Water Treatment Works A supplies up to 55 million litres of potable water everyday to over 195,400 people in Halifax and Calderdale. The data for THM4 concentrations, residual chorine and pH were not available between January 1999 - April 1999 and January 2003 - April 2003. The only data on water temperature were available during the period June 2001 - December 2002.

2.3.1 THM concentration, pH and residual chlorine (January 1998-June 2007)

Figure 2.3, shows the total THM4 concentrations and pH from January 1998 - June 2007. A total of 549 samples was analysed during this period. The mean concentration of the THM4 across the whole period was 42.0 µg/l (σ_{n-1}=15.2 µg/l; range of 8.4 - 108.7 µg/l). During the period January 1998 - December 1999, the maximum concentration of THM4 was observed in June 1998 (108.7 µg/l) and the lowest in December 1999 (21.6 µg/l), with a mean value of 56.4 µg/l (σ_{n-1}=16.9 µg/l). However, after January 2000, the highest concentration of THM4 observed was in August 2002 (76.3 µg/l) with the lowest observed in January 2004 (8.4 µg/l). The mean THM4 concentration was 37.7 µg/l (σ_{n-1}=12.1 µg/l) for the period between January 2000 - June 2007. The reduction in THM4 concentrations was most likely owing to the improvements in water treatment processes introduced in order to conform with the UK regulations (2000).

The levels of THM4 were observed to fluctuate seasonally with highs during summer and lows during the winter. After January 2000, the mean THM4 concentrations during the seven 'summer' periods (June - September) were 48.4 µg/l (σ_{n-1}=8.2 µg/l; range of 26.6 - 76.3 µg/l), while during the 'winter' periods (December - March), the THM4 concentrations had a mean of 27.3 µg/l (σ_{n-1}=4.7 µg/l; range of 8.4 - 40.3 µg/l). The mean pH value was 8.0 (σ_{n-1}=0.5; range 6.7 - 9.6) for the period between January 1998 - June 2006. The residual chlorine levels at the treatment works were between 0.1 and 0.5 mg/l with a mean of 0.3 mg/l for the 512 samples analysed during the same period.

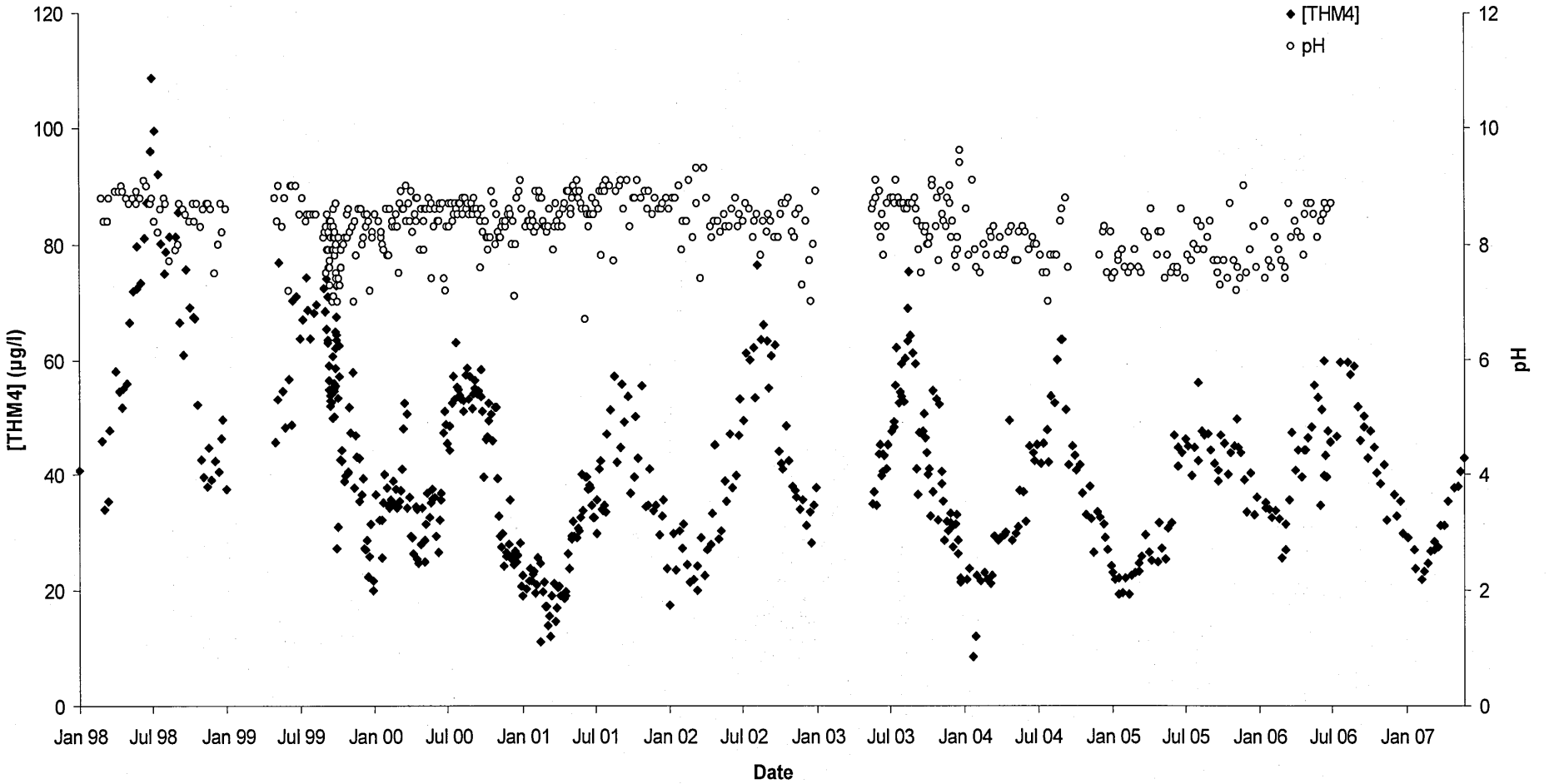


Figure 2.3: The concentrations measured for THM4 during the period January 1998 - June 2007 and pH for the period between January 1998 - June 2006 for the Water Treatment Works A located in Yorkshire, England. No data was available between January 1999 - April 1999 and January 2003 - April 2003.

2.3.2 A more detailed study of THM concentrations (July 2001 - December 2002)

During the period July 2001 - December 2002, the influence of temperature and pH on the levels of THMs was examined in more detail. The mean THM4 concentration was 40.5 µg/l (σ_{n-1}=13.0 µg/l) with a range of 17.3 - 76.3 µg/l. During the same period, the pH ranged from 7.0 - 9.3 with a mean of 8.5 (σ_{n-1}= 0.4). Water temperature fluctuated between 4.0 and 17.0 °C, with a mean value of 10.5 °C (σ_{n-1}= 3.2 °C).

Temperature

The influence of temperature on the levels of THMs was examined by plotting a graph with a 5 point moving average correlation, a procedure used by Whitaker and colleagues (Whitaker *et al.*, 2003). The graph is shown in Figure 2.4 A. The general trend showed that an increase in water temperature resulted in an increase in THM4 concentrations. During the winter period, between December 2001 and March 2002, the waters were generally colder (mean 7.7 °C; σ_{n-1}=1.4 °C; range 4.0 - 9.0 °C), and hence lower THM4 concentrations were observed (mean 26.9 µg/l; σ_{n-1}=5.3 µg/l; range 17.3 -35.4 µg/l). During the summer period of June 2002 - September 2002, higher water temperatures were observed (mean 13.2 °C; σ_{n-1}=2.7 °C; range 9.0 - 17.0 °C). The THM4 concentrations were also higher (mean 56.4 µg/l; σ_{n-1}=9.9 µg/l; range 37.8 - 76.3 µg/l).

Figure 2.4 B illustrates the best-fit line, found through least square fitting, for THM4 concentrations and temperature (R^2 = 0.2353). The data were very noisy, possibly because of other parameters such as the presence of NOM and bromide ions which can also influence the formation of THMs (Amy *et al.*, 1998; Carlson *et al.*, 1998; Chang *et al.*, 2008; Cowman *et al.*, 1996; Nikolaou *et al.*, 2004b; Westerhoff, 2006; Xie, 2003; Yang *et al.*, 2007).

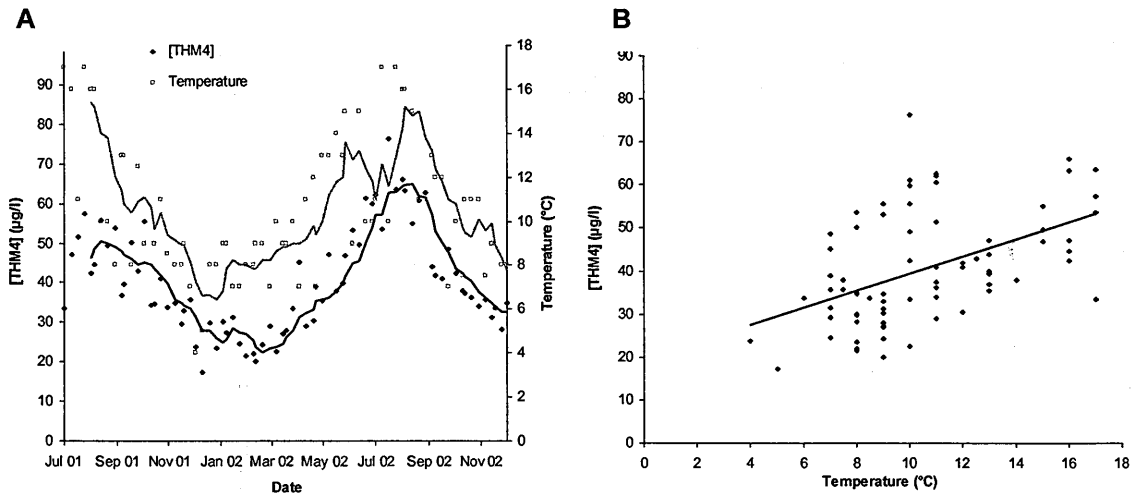


Figure 2.4: A) A correlation plot between temperature and THM4 concentrations using moving averages for the period June 2001 - December 2002 and B) A plot of the results from A) with a line of best fit found through least squares fitting.

pH

The influence of pH on THM4 concentrations was also examined in more detail by plotting a graph of the pH and THM4 concentrations with a moving average correlation. As can be seen in Figure 2.5 A, pH remained relatively stable at a mean of 8.5 (σ_{n-1}=0.4; range 7.0 - 9.3). As can be seen in Figure 2.5 B, there was no correlation between THM4 and pH, with the data available.

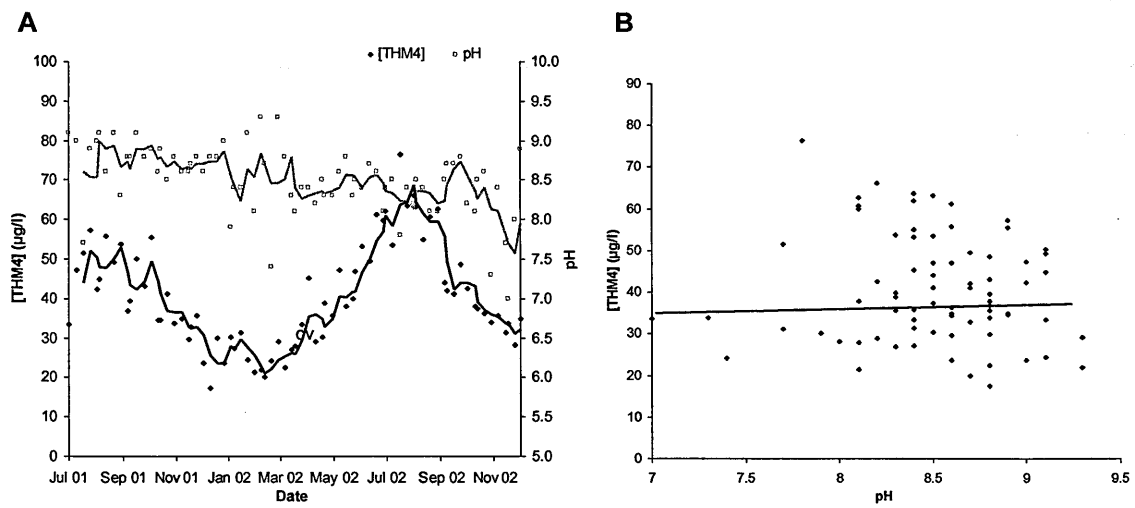


Figure 2.5: The correlation plot between pH and THM4 concentrations using moving averages for the period June 2001 - December 2002 and B) A plot of the results from A) with a line of best fit found through least squares fitting.

Data for the individual THM species were only available between June 2006 - June 2007 (n=44). During this period, the THM4 concentrations fluctuated between 21.8 µg/l and 59.6 µg/l with a mean of 38.4 µg/l (σ_{n-1}=10.1 µg/l). Whereas, $CHCl_3$ concentrations had a mean of 30.5 µg/l and ranged between 16.5 - 50.2 µg/l (σ_{n-1}=9.2 µg/l). $CHCl_3$ accounted for 78.7 % (68.7 - 84.4 %) of the total quantity of THM4 in the water. $CHCl_2Br$ was the second most abundant THM present with a mean of 6.5 µg/l (σ_{n-1}=1.3 µg/l; range 4.3 - 8.6 µg/l) and accounted for around 17.4 % (13.4 - 21.1 %) of the total THM4. This was followed by $CHClBr_2$ (mean 1.4 µg/l) and $CHBr_3$ (mean 0.3 µg/l) respectively.

2.4 Service Reservoir X

Service Reservoir X was a few miles downstream of the Water Treatment Works A. No data were available for any of the three variables (pH, THM4 and temperature) between January 2003 - April 2003 and November 2004 - April 2005. Additionally, no THM4 data were available between January 1999 - April 1999. During the period June 2001 - December 2002, additional data on water temperature levels were available.

As with the Water Treatment Works A, the variability in THM4 concentrations for the period January 1998 - June 2007 and pH levels for the period January 1998 - June 2006 are considered at this site, as illustrated in Figure 2.6.

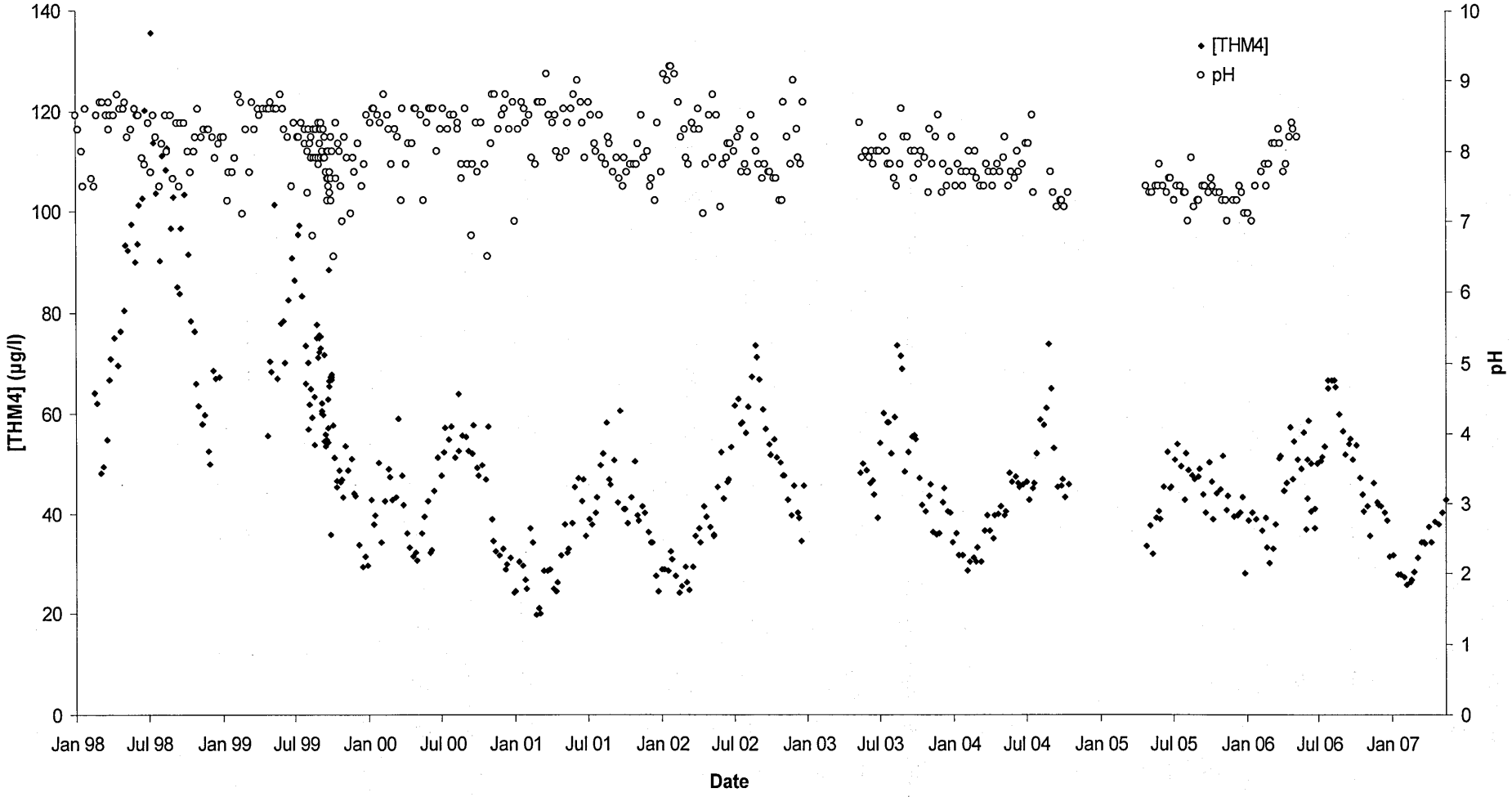


Figure 2.6: The concentrations measured for THM4 for the period January 1998 - June 2007 and pH for the period between January 1998 - June 2006 at the Service Reservoir X. No data were available between January 1999 - April 1999 (THM4), January 2003 - April 2003 and November 2004 - April 2005 (for both variables).

2.4.1 THM concentration, pH and residual chlorine (January 1998 - June 2007)

Throughout the whole period a mean concentration of 50.2 µg/l (range 19.8 - 135.7 µg/l; σ_{n-1}=18.3 µg/l) was found for THM4. As with the Water Treatment Works, before January 2000, the highest THM4 concentrations were observed during the summer period of June - September with a maximum of 135.7 µg/l (July 1998) and a minimum of 29.5 µg/l during the winter (December 1999). After January 2000, the maximum and minimum THM4 concentrations observed were 77.4 µg/l and 19.8 µg/l respectively. The mean value during this period was 43.2 µg/l (σ_{n-1}=10.7 µg/l). The pH levels ranged between 6.5 and 9.2 for the whole period January 1998 - June 2006 with a mean value of 8.0 (σ_{n-1}=0.5). During the period June 2001 - December 2002, the water temperature fluctuated between a low of 4.0 °C (December 2002) and a high of 16.0 °C (August 2001 and July 2002) with a mean temperature of 10.8 °C (σ_{n-1}=2.9 °C). The residual chlorine levels at the treatment works were between 0.05 mg/l and 0.60 mg/l with a mean of 0.11 mg/l between January 1998 - June 2007; however, no data were available between June 2001 - December 2003.

For the period between June 2006 - June 2007, where individual THM data were available, the THM4 levels fluctuated between 25.9 µg/l and 66.6 µg/l with a mean of 43.0 µg/l (n=50). $CHCl_3$ concentrations were found to be between 18.6 - 56.2 µg/l, with a mean of 33.7 µg/l. $CHCl_3$ accounted for 77.6 % (69.4 - 84.5 %) of the THMs present in the reservoir. The second most abundant THM present was $CHCl_2Br$ (mean 7.6 µg/l), followed by $CHClBr_2$ (mean 1.6 µg/l) and $CHBr_3$ (mean 0.4 µg/l).

2.5 Summary

The above study would indicate that the THM4 concentrations at the customers' tap would have been below 100 µg/l for the period between January 2000 and June 2007. YWS would have complied with its legal obligations to meet the regulated THM4 levels. This

finding is confirmed by a report from YWS, where it stated that it has "demonstrated a 100 % compliance in achieving the THM4 regulation between 2003 - 2007" (Yorkshire Water, 2008). In 2008, the DWI has also confirmed its compliance with THM4 concentrations ranging between 3.3 and 87.1 µg/l, in the 594 tests analysed (DWI, 2009).

Service Reservoirs

This study shows that the THM4 concentrations, during the period June 2006 - June 2007, in some of the service reservoirs (Site 6) were close to the regulated limit of a maximum of 100 µg/l in single sample (96.6 µg/l). Higher concentrations of THMs in service reservoirs than water treatment works was expected. For example, Lebel *et al.* (1997) reported that the concentration of the THMs increased within the distribution system. They reported that THM4 were found at 24.8 µg/l, immediately after treatment, and at 37.5, 48.4, and 61.4 µg/l at an increasing distance, and hence increasing contact time, from the treatment plant. Increases in THM concentrations have also been reported by Nikolaou and colleagues in a study of river water samples (Nikolaou *et al.*, 2004b). This increase was because of the on-going reaction of the residual chorine with the NOM already present in the water (Nikolaou *et al.*, 2004b).

The most abundant THM in most of the service reservoirs was $CHCl_3$. $CHCl_2Br$ was the most second most abundant, followed by $CHClBr_2$ and $CHBr_3$, respectively.

Water Treatment Works A and the Service Reservoir X

A comparison of the range in the levels of pH, residual chlorine, temperature and THM concentrations between the Water Treatment Works A and the Service Reservoir X, has been summarised in Table 2.1. As expected, the results for the pH and temperature were similar. However, the THM4 concentrations in the Service Reservoir X were approximately 20 % higher than that found in the Water Treatment Works A. This was probably because of the ongoing reactions of residual chlorine with the natural organic matter already

present in the water, as the residual chlorine levels were also observed to have reduced. The reduction of residual chlorine levels could also be because of natural decay.

Table 2.1: Comparison of the pH, residual chlorine, temperature, THM4 concentrations and $CHCl_3$ concentrations between the Water Treatment Works A and the Service Reservoir X.

	Water Treatment Works A	**Service Reservoir X**
pH [1]	8.0 (6.7 - 9.6)	8.0 (6.5 - 9.2)
Residual chlorine [1] (mg/l)	0.3 (0.1 - 0.5)	0.1 (0.05 - 0.6)
Temperature [2] (°C)	10.5 (4.0 - 17.0)	10.7 (4.0 - 16.0)
THM4 [4] (µg/l)	42.0 (8.4 - 108.7)	50.2 (19.8 - 135.7)
THM4 [5] (µg/l)	37.7 (8.4 - 76.3)	43.3 (19.8 - 77.4)
$CHCl_3$ [3] (µg/l)	30.0 (16.5 - 50.2)	33.7 (18.6 - 56.2)
$CHCl_3$ [3] (%)	78.7 (68.7 - 84.4)	77.6 (69.4 - 84.5)

[1] *January 1998 - June 2006,*
[2] *July 2001 - December 2002,*
[3] *June 2006 - June 2007,*
[4] *January 1998 - June 2007,*
[5] *January 2000 - June 2007.*

The THM levels reported in this study were similar to another study of water systems in the UK. Between 1992 - 1998, Whitaker *et al.* (2003) reported annual mean THM4 concentrations of 48.6, 33.7 and 48.7 µg/l in three water treatments works across Northern and Central England (Whitaker *et al.*, 2003). They also reported $CHCl_3$ as the most abundant THM, with an annual mean concentration of 17.9, 36.1 and 38.1 µg/l for the three treatment works, respectively. Similar seasonal fluctuations of THMs levels were also observed in their paper and attributed to temperature variations. Levels of pH and residual chlorine were not reported. In another study by Keegan *et al.*, the THM4 concentrations from a water company in the north west of England showed a mean concentration of 47.6 µg/l (range 6.6 - 142.2 µg/l) between 1992 - 1996 (Keegan *et al.*, 2001).

pH

The mean pH levels in the YWS's distribution system were generally around 8. There are no health risks associated with consuming water that is slightly acidic or alkaline, hence the WHO does not have any health-based guideline values for pH (WHO, 2006). However, the optimum pH for operational and aesthetic purposes has been recommended to be in the range 6.5 - 9.5 (WHO, 2004a; WHO, 2006). The UK Water quality regulations require the monitoring of pH at a guide value range of 6.5 - 9.5 (DWI, 2000). pH is one of the most important operational water quality parameters. Studies have shown that THM4 concentrations increase with an increase in pH (El-Dib *et al.*, 1995; Xie, 2003). Higher pH levels can also increase the solubility of some metals such as zinc, and can influence the aesthetic quality of the water. Furthermore, lower pH values can lead to pipe corrosion during water distribution (DWI, 2010b; Gray, 2008). The levels of pH in both the Water Treatment Work A and the Service Reservoir X were almost always found within the desired range.

Residual chlorine

As discussed previously in Section 1.7.5.2 a certain level of residual chlorine is desired in the distribution system to prevent the re-growth of microorganisms. The World Health Organization (WHO) has established a guideline value of 5 mg/l residual chlorine in drinking water. The WHO also recommends a free residual chlorine concentration of at least 0.5 mg/l after a contact time of 30 minutes at a pH < 8 (Twort *et al.*, 2000a; WCC, 2008; WHO, 2006). The water companies in the UK are required to analyse the residual chlorine in the water treatment works, in service reservoirs and at consumer's taps, although the value for residual disinfectant is not regulated (DWI, 2000). DWI reports that water companies typically keep residual chlorine levels under 0.5 µg/l, as found in this study (DWI, 2010a). The levels of residual chlorine reported in other regions globally were between 0.5 - 0.8 µg/l (Duong *et al.*, 2003; El-Shafy *et al.*, 2000; Galal-Gorchev, 1996).

Temperature

The temperature levels in Yorkshire Water's distribution system were expected to fluctuate because of seasonal temperature variation, *i.e.* higher in summer and lower in winter. In line with previous research, the findings showed that higher THM4 concentrations were associated with seasonal fluctuations and higher temperatures (Dojlido *et al.*, 1999; El-Shafy *et al.*, 2000). They attributed the increase in THM4 to temperature influencing the rate of reaction between chlorine and NOM, during the formation of THMs. However, it is also possible that during the summer seasons, the concentrations and types of NOM were greater leading to more THM formation.

There are several other parameters that influence the formation of THMs, such as the levels and composition of NOMs, bromide concentrations and chlorine dose, as summarised in Chapter 1. Their influence on the formation of THMs was not investigated in this chapter, because of the absence of any data.

2.6 Conclusions

A review of the data has shown, that in agreement with published reports, that the THM4 concentrations in YWS's distribution system would have been below 100 µg/l for the period between January 2000 and June 2007, and would therefore would have complied with its legal obligations. However, this study has also shown that this is a highly dynamic environment and the concentrations in some service reservoirs have approached the regulated levels. During these events, a near-real time monitoring system would have been valuable. Such a system could have provided an early-warning indication of the increase in THM4 levels in the service reservoirs or water treatment works. In these cases, immediate remedial actions to reduce such high THMs levels could be implemented. This could include the use of granular activated carbon (GAC) or aeration technologies. This study has also provided a valuable insight into the temporal variations in many of the parameters that are important in the formation of disinfection by products.

Based on the findings from this study, and the particular water sources in this geographic region, the primary analyte will be $CHCl_3$; however, as all of the four THMs are regulated, and water sources throughout the UK will vary, any method developed should be capable of monitoring all four THMs. This thesis will report on investigations to develop methods that have the potential to be translated for near-real time monitoring of THMs, as described in Chapter 4.

3. Materials and analytical methods

3.1 Materials and methods for THM analyses

3.1.1 Glassware and laboratory equipment

Standard laboratory glass beakers (50, 100 and 200 ml) and volumetric flasks (4, 10, 25, 50, 100 and 500 ml) were used in the experiments. Prior to use, the glassware was soaked in Decon90, rinsed with ultrapure water, and dried in an oven. Glass micro-syringes (10, 25, 50 and 100 µl; Gilson Scientific Ltd) and a 5 ml automatic pipetter (Hamilton) with clean plastic pipettes tips were also utilised. The micro-syringes were washed with methanol and ultrapure water at least 10 times before each use.

The crimp-seal glass headspace vials (2, 10 and 20 ml) were purchased from Chromacol UK. Blue and gold crimp magnetic vial caps with PTFE/Silicone septa were also procured from Chromacol UK. The 10 ml and 20 ml glass vials were re-used after cleaning, as reported above.

3.1.2 Standards and reagents

A calibration mix containing four THMs (*i.e.* $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) at 200 µg/ml of each in methanol, was obtained from Supelco UK. The calibration standards were stored in a fridge at 4 °C. Deionised ultrapure water (18 Ω) was prepared from tap water by using an Elga Purelab Ultra water purification system. At Cranfield University, ultrapure water (18 Ω) was obtained from a Millipore water purification system (used in Chapter 5 and 6). Helium, at BIP Grade (Air Products) and nitrogen at Grade 4.6 (99.996 %; BOC), were used in the gas chromatography instruments.

3.1.3 Sample preparation and chromatographic parameters

The THMs were analysed using various GC instrumentation and many of the analytical parameters were optimised in Chapter 4. Photographs of the instrumentation used here are provided in Appendix 6. The optimised parameters, which were used for all further studies (such as in Chapter 6), are reported here.

3.1.3.1 Headspace - gas chromatograph - mass spectrometry (HS-GC-MS)

A Varian CP-3800 gas chromatograph interfaced with a Saturn-2000 ion trap mass spectrometer, and a CTC Combi Pal autosampler were used in the experiments for the analyses of THMs.

For the headspace extraction, 10 ml headspace vials containing solution were incubated at a temperature of 60 °C for 30 minutes. The syringe assembly unit, which was fitted with a 1 ml headspace syringe (Hamilton 1001), was heated and maintained at 60 °C throughout. The autosampler conditions are summarised in Table 3.1.

Table 3.1: The CTC autosampler parameters used for the analyses of THMs.

Parameter	Value
Syringe type	1.0 ml headspace
Sample volume (µl)	500
Incubation temp (°C)	60
Incubation time (min)	30
Agitator speed (rpm)	500
Agitator on (s)	4
Agitator off (s)	2
Syringe temp (°C)	60
Fill up speed (µl/s)	100
Pull up delay (ms)	500
Injection speed (µl/s)	250
Pre-injection delay (ms)	500
Post-injection delay (ms)	500
Syringe flush time with Helium (s)	30

An aliquot (500 µl) of the headspace was extracted using the heated syringe, and injected in to the GC inlet at 250 °C, with a spilt ratio of 10:1. A 3.4 mm id (split /splitless with single taper; SGE Europe Ltd) liner was used in the inlet. Separation of the analytes was achieved using a BPX5 column (30 m × 0.25 mm id × 0.25 µm; SGE Europe Ltd). At injection, the initial GC oven temperature was set at 45 °C and held for 2 minutes. The temperature was then raised at a rate of 10 °C/min to 85 °C. The helium carrier gas flow was held at 1 ml/min throughout the run.

In the mass spectrometer, the trap temperature was set to 200 °C, the manifold temperature was 100 °C, the transfer-line temperature was 280 °C, and the electron impact ionisation energy (EI) was set at 70 eV. Full scan mode was used, at a scan rate of 0.29 scans/s, with a mass range of *m/z* 40 - 350.

3.1.3.2 Headspace - solid phase micro extraction - gas chromatograph - mass spectrometry (HS-SPME-GC-MS)

The THM analyses were performed using a Supelco SPME fibre assembly unit fitted with a 75 µm carboxen/polydimethylsiloxane fibre (CAR/PDMS). The fibre was conditioned by inserting it into the GC-injector for 1 hour at 300 °C, in accordance with the manufacturer's guidelines.

The SPME fibre was exposed to the headspace above the sample for 5 minutes. During the extraction, the vials were held at 60 °C and agitated at 500 rpm. The fibre was immediately retracted back into the needle and transferred to the GC injection port. The fibre was thermally desorbed in to the inlet at 250 °C, for 5 minutes.

All headspace, GC and MS parameters were the same as those described in Section 3.1.3.1, except that, in this case, a narrow-bore inlet liner (0.5 mm id, straight-through; SGE Europe Ltd) was used.

3.1.3.3 Headspace - gas chromatograph - micro electron capture detector (HS-GC-μECD)

An Agilent 6890 N gas chromatograph fitted with a micro electron capture detector (GC-μECD) and a CTC CombiPal autosampler was used in the experiments. All the headspace and GC parameters were the same as those reported in Section 3.1.3.1. However, in this case, the inlet contained a tapered liner (4.0 mm id split/splitless, tapered; SGE Europe Ltd). The detector temperature was set at 250 °C and the nitrogen make-up gas flowed at 30 ml/min through the detector.

3.1.3.4 Liquid-liquid extraction - gas chromatograph - micro electron capture detector (LLE-GC-μECD)

An Agilent 6890 N GC-μECD fitted with an Agilent 7673 liquid autosampler was utilised for the experiments. The liquid-liquid extraction of the THMs using MTBE has been described in Appendix 2. Using a 10 μl liquid syringe, 1 μl was injected using a 10:1 split ratio. The GC inlet was isothermally set at 250 °C and a tapered inlet liner (4.0 mm id, split/splitless, tapered; SGE Europe Ltd) was used. The autosampler parameters used are summarised in Table 3.2.

Separation of the analytes was performed on a BPX5 GC column (30 m × 0.25 mm id × 0.25 μm; SGE Europe Ltd). The initial GC oven temperature was set at 35 °C and held for 2 minutes. The temperature was then raised at a rate of 5 °C/min to 90 °C. The temperature was then further ramped to 260 °C, at a rate of 30 °C/min, and held for 2 minutes. A constant flow rate of carrier gas (1 ml/min) was held throughout the run. The detector temperature was set at 250 °C and the nitrogen make-up gas flowed at 30 ml/min through the detector.

Table 3.2: The parameters of the Agilent 7673 autosampler used for the analyses of THMs using liquid injection.

Parameter	Value
Syringe	10 µl liquid
Injection volume (µl)	1
Fill up speed (µl/s)	100
Pull up delay (ms)	500
Injection speed (µl/s)	250
Pre-injection wash	Hexane, 3 times
Post-injection wash	Methanol, 3 times
Pre-injection delay (ms)	500
Post-injection delay (ms)	500

3.1.4 Data processing and quantitation

MASSTransit Software (Version 3, Palisade Corp) was used to convert the Varian GC-MS data files so that they could be viewed by the Agilent ChemStation software. The Agilent Enhanced ChemStation software (G1710EA) was then used for data handling and processing, including the calculation of any peak areas, peak heights and signal to noise ratios in the subsequent chapters.

Total ion chromatograms were obtained on the GC-MS. Quantitation was performed using partially reconstructed ion chromatograms (RIC) of diagnostic ions. The ions used for each of the THMs were: *m/z* 83 ($CHCl_3$ and $CHCl_2Br$), *m/z* 129 ($CHClBr_2$) and *m/z* 173 ($CHBr_3$). The *m/z* 83 ion is characteristic of the fragment $CHCl_2^+$, *m/z* 129 is characteristic of the fragment $CHBrCl^+$, and *m/z* 173 is characteristic of $CHBr_2^+$.

The presence of THMs in the chromatograms obtained by the GC-µECD were inferred by comparing retention times with those from peaks previously identified from THM standards. The concentrations of the THMs in the samples were determined by measuring peak areas and relating them to the calibration curves obtained from known quantities of standards.

3.1.5 Procedures to ensure analytical accuracy

In order to ensure reliable results, a number of procedures were adopted prior to each investigation. The linearity of the method was regularly tested by running a series of calibration standards (0, 10, 25, 50, 100 µg/l per THM) prior to every investigation, or at least within one week of the analysis. Procedural blanks, containing only ultrapure water (THM4 concentration of 0 µg/l) were also analysed to ensure there were no sources of instrument or procedural contamination. Clean, empty vials were also used as system blanks to ensure there was no contamination and no carry-over from the headspace syringe system. Spiked treated water samples were analysed in conjunction with un-spiked samples to ascertain the accuracy of the analytical method used.

3.2 Materials and methods for HAA analyses

3.2.1 Glassware and laboratory equipment

Standard laboratory glass beakers (50 and 100 ml), clear glass volumetric flasks (10, 100, 500 ml) and 200 µl amber glass vials were used in the experiments. Glass micro-syringes (10, 50 and 100 µl; Gilson Scientific Ltd) and a 5 ml automatic pipetter (Hamilton) were also used. All the glassware was cleaned as reported in Section 3.1.1.

3.2.2 Standards and reagents

A HAA6 calibration mix containing monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA) was purchased from Supelco UK. Each of the HAAs was present at a concentration of 2,000 µg/ml in methyl tert-butyl ether (MTBE). A HAA9 calibration mix containing the six HAAs above, as well as bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TBAA) was also obtained from Supelco UK. Once again, the concentration of each HAA was 2000

µg/ml of each in MTBE. The two HAA standards were used at different stages of the analytical work, as reported in Chapter 5.

The following compounds were obtained by the Cranfield Water Science Institute, at Cranfield University, for sample preparation (Bougeard, 2009). Sulphuric acid (H_2SO_4), copper sulphate ($CuSO_4$), sodium sulphate (Na_2SO_4), methanol and MTBE were purchased from Sigma Aldrich UK and used without further purification. The internal standard, 1,2,3 trichloropropane (200 µg/ml in methanol), was purchased from Supelco UK. The ultrapure water and purity of the instrument gases used is reported in Section 3.1.2.

3.2.3 Sample preparation

The sample preparation procedure for the extraction and derivatisation of HAAs, to its respective methyl esters, used a modified version of USEPA Method 552.2 (1995) developed by Tung and colleagues (Tung *et al.*, 2006). Members of the Cranfield Water Science Institute, at Cranfield University, performed all sample preparation and their methodology is described below (Bougeard, 2009):

A 30 ml volume of water sample was extracted with 3 ml of MTBE spiked with an internal standard (1,2,3 trichloropropane) at 1000 µg/l. Concentrated sulphuric acid (1.5 ml) and Na_2SO_4 (12 g) were then added to the vials and shaken for 3 minutes. A volume of the upper MTBE layer (2.5 ml) was taken out, methylated by adding 1 ml of 10 % sulphuric acid in methanol and kept at 50 °C for 2 hours. The resulting solution was washed with 1 ml of 10 % Na_2SO_4 solution. The upper layer, containing the methylated extracts, was then transferred to 2 ml vials and stored at -18 °C prior to analysis. Analyses were performed within 14 days of extraction.

A series of calibration standards at 0, 10, 25, 50, 75 and 100 µg/l was prepared by diluting the HAA calibration mix with ultrapure water. Procedural blanks containing ultrapure water

were used to determine the level of background contamination. Solvent blanks, *i.e.* vials containing just the solvent (MTBE), were also regularly analysed to ensure there was no contamination from the solvents and no possible carry-over from the injection source. All derivatised HAA calibration standards and samples for each investigation were prepared at the same time and derivatised simultaneously using the same derivatisation process and reagents to ensure consistency. A single point internal standard method was used for the quantitation of HAAs. The compound 1,2,3-trichloropropane was used as the internal standard at a concentration of 1,000 µg/l.

A schematic of this method is provided in Appendix 3.

3.2.4 Chromatographic parameters

Several chromatographic parameters were optimised in Chapter 5 and the findings from those investigations are reported here, and are the same for those used in all further analysis of HAAs (as in Chapter 7).

3.2.4.1 Autosampler parameters

Either a CTC CombiPal autosampler or an Agilent 7673 automatic liquid sampler were used for the liquid injections of the derivatised HAAs. The autosampler parameters used on all the instruments are summarised in Table 3.3.

Table 3.3: The autosampler parameters used for the analyses of HAAs.

Type	Values
Syringe	10 µl liquid
Injection volume (µl)	1
Fill up speed (µl/s	100
Pull up delay (ms)	500
Injection speed (µl/s)	250
Pre injection wash	Hexane, 3 times
Post injection wash	Methanol, 3 times
Pre injection delay (ms)	500
Post injection delay (ms)	500

3.2.4.2 Gas chromatograph - micro electron capture detector (GC-µECD)

An Agilent 6890 N gas chromatograph, with a micro electron capture detector (µECD) and a CTC CombiPal autosampler, was used for the HAA analyses. An injection volume of 1 µl was introduced *via* a 5:1 split ratio with the inlet temperature set at 200 °C. An Agilent Focus liner (4.0 mm id split/splitless, tapered) with a glass wool insert was used in the inlet. Separation was performed on a DB-5.625 column (30 m × 0.25 mm id × 0.25 µm; J&W). The initial GC oven temperature was set at 35 °C and held for 2 minutes. The temperature was then raised at a rate of 5 °C/min to 220 °C. A constant carrier flow rate of 1.1 ml/min was used. The µECD temperature was set at 230 °C and nitrogen make-up gas flowed through the detector at 30 ml/min.

3.2.4.3 Two-dimensional gas chromatograph - time of flight mass spectrometry (GC×GC-ToFMS)

HAAs were also analysed by comprehensive, two-dimensional gas chromatography, which comprised of an Agilent 6890 N gas chromatograph fitted with a GC×GC cryogenic modulator (Zoex UK Ltd) coupled to a Leco Pegasus IV time-of-flight mass spectrometer and a CTC CombiPal autosampler (GC×GC-ToFMS). The GC injector was held at 200 °C and operated in splitless mode with a column flow rate of 1.0 ml/min. For orthogonal

separation, a non polar SGE BPX5 (30 m × 0.25 mm id × 0.25 µm) column was used as the first column and a more polar SGE BPX50 (1.8 m × 0.1 mm id × 0.1 µm) column was used as the second column. The GC oven was held at 35 °C for 1 minute, and then ramped to 220 °C at a rate of 5 °C/min, before being held at that temperature for a further 1 minute. The second column oven was kept 15 °C above the GC oven temperature. The modulation time was 4 seconds and the modulator was held at 30 °C above the main oven temperature. Cryogenic cooling at the modulator was enabled by passing nitrogen gas through a liquid nitrogen dewar. The mass spectra were acquired in electron ionisation mode (70 eV) with an acquisition rate of 133 Hz across the mass range *m/z* 33 to 400.

3.2.4.4 Gas chromatograph - mass spectrometry in standard electron impact ionisation mode (GC-MS (EI))

An Agilent 6890 N gas chromatograph coupled to a 5973 quadrupole mass spectrometer and equipped with an Agilent 7673 liquid autosampler was utilised for HAA analyses. All the GC parameters used were the same as those reported in Section 3.2.4.1. A constant carrier flow rate of helium at 1 ml/min was used. The transfer line temperature was maintained at 280 °C, while the source and quadrupole temperatures were set at 230 °C and 150 °C, respectively. In full scan mode, the mass spectra were obtained at electron impact energies of 70 eV and over mass range of *m/z* 33 - 500. In selected ion monitoring (SIM) mode, the ions *m/z* 59 and 75 were selected, with a dwell time of 80 ms.

3.2.4.5 Gas chromatograph - mass spectrometry in electron capture negative chemical ionisation mode (GC-MS (ECNI))

The analyses were performed on an Agilent 7890 N interfaced with a 5975 quadrupole mass spectrometer and a CTC CombiPal autosampler. All other parameters used were the same as those reported in Section 3.2.4.1. However, in this mode of operation, the initial oven temperature was set at 35 °C, held for 2 minutes, followed by a 5 °C/min temperature ramp to 115 °C. The oven was then ramped at a rate of 25 °C/min to 220 °C.

The transfer-line temperature was maintained at 250 °C. The mass spectrometer was operated in electron capture negative chemical ionisation mode, with the ionisation energy of 70 eV. Isobutane was used as the reagent gas, at a flow rate of 40 ml/min. The source temperature and quadrupole temperatures were both set at 150 °C. The mass spectra were acquired in selected ion monitoring (SIM) mode using the ions *m/z* 35 and 81, at a dwell time of 80 ms.

3.2.5 Data processing and quantitation

The data from the μECD and MS were processed using the Agilent Enhanced ChemStation Software (G1710EA). The processing of the GC×GC-ToFMS data was performed on the Leco ChromaTOF Software (Version 2.25). Both of these softwares were used to also calculate the peak areas, peak heights and signal to noise ratios in the subsequent chapters.

The analyses of HAAs by GC-MS (EI) and GC×GC-ToFMS, run in full scan, produced total ion chromatograms and the fragment ions, *m/z* 59 and 75 were then selected for quantitation. The *m/z* 59 ion is the base peak for the HAA methylesters and *m/z* 75 is the base peak for the internal standard, 1,2,3 trichloropropane. The *m/z* 59 ion is characteristic of the $COOCH_3^+$ fragment obtained from the HAAs and the *m/z* 75 ion is characteristic of the $C_3H_4Cl^+$ fragment from the IS.

In ECNI mode, single ion chromatograms were produced of the ions *m/z* 35 and 81. The ion *m/z* 35 was used for the quantitation of the chlorinated HAAs and internal standard and *m/z* 81 was used for the brominated HAAs. The *m/z* 35 ion is characteristic of the Cl^- fragment obtained from the chlorinated HAAs and IS, while the *m/z* 81 ion is characteristic of the Br^- fragment from the brominated HAAs.

HAA peaks from the GC-μECD were identified by comparing the retention times with those obtained from calibration standards that had been previously investigated with the same instrument and under identical conditions.

4. Development and optimisation of methods for the analysis of trihalomethanes (THMs)

4.1 Introduction

Trihalomethanes (THMs) were the first disinfection by-products (DBPs) to be discovered in drinking water (Rook, 1974). THMs consist of four volatile compounds to include $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$. The total concentration of these four THMs in drinking waters are regulated in the UK, at <100 µg/l, at the customers' tap (DWI, 2000). To meet this regulation the current industrial practice is manually to collect the required samples, at regular periods and at known locations, which are then sent to specialist analytical laboratories for analysis.

Chapter 1 summarised the many methods for the analysis of THMs that have been reported in the literature. Accredited laboratories would use the established USEPA methods for the analyses of THMs, such as the purge and trap-GC-MS and liquid-liquid extraction-GC-µECD (USEPA, 1979a; USEPA, 1979b; USEPA, 1990; USEPA, 1995c; USEPA, 1996b; USEPA, 1998a). As was also stated, such methods are primarily restricted to traditional analytical laboratories and would be impractical for real time or near-real time monitoring of THM levels within the UK water distribution systems. In the case of the GC-µECD the requirement to have a permit for the radioactive ^{63}Ni source can be limiting, if required beyond a standard analytical laboratory. In addition, as illustrated in Chapter 2, the potable water system is highly dynamic and could benefit from real time monitoring to manage actively the DBP concentrations and maintain them below the regulatory levels. The possibility also exists for the use of THM concentrations as predictors for HAA concentrations (Villanueva *et al.*, 2003).

The aim of this chapter is to evaluate and optimise existing analytical methods that would be suitable for translation to near real-time monitoring of THM concentrations. The performances of HS-GC-MS, HS-SPME-GC-MS, HS-GC-μECD and LLE-GC-μECD were all evaluated in terms of their linearity, repeatability, accuracy and LODs, against published methods. Their viability for monitoring purposes was also evaluated.

4.2 Materials and methods

The HS-GC-MS and HS-SPME-GC-MS analyses were performed on a Varian Saturn 2000 ion trap GC-MS fitted with a CTC autosampler, as this best represented the mass spectrometer technologies being developed within PSSRI. The HS-GC-μECD and LLE-GC-μECD analysis were performed on an Agilent 6890 GC. The final instrumental conditions, the materials and experimental parameters have been reported in full in Chapter 3.

A calibration mix containing four THMs (*i.e.* $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) at 200 μg/ml of each in methanol, was obtained from Supelco UK. This section illustrates the importance of characterising and evaluating all procedures including the preparation of calibration standards.

The original procedure for the preparation of the THMs calibration standards was obtained from the Cranfield Water Science Institute at Cranfield University. As shown in Figure 4.1, this procedure was found to result in the loss of the more volatile THMs during the preparation of the standards.

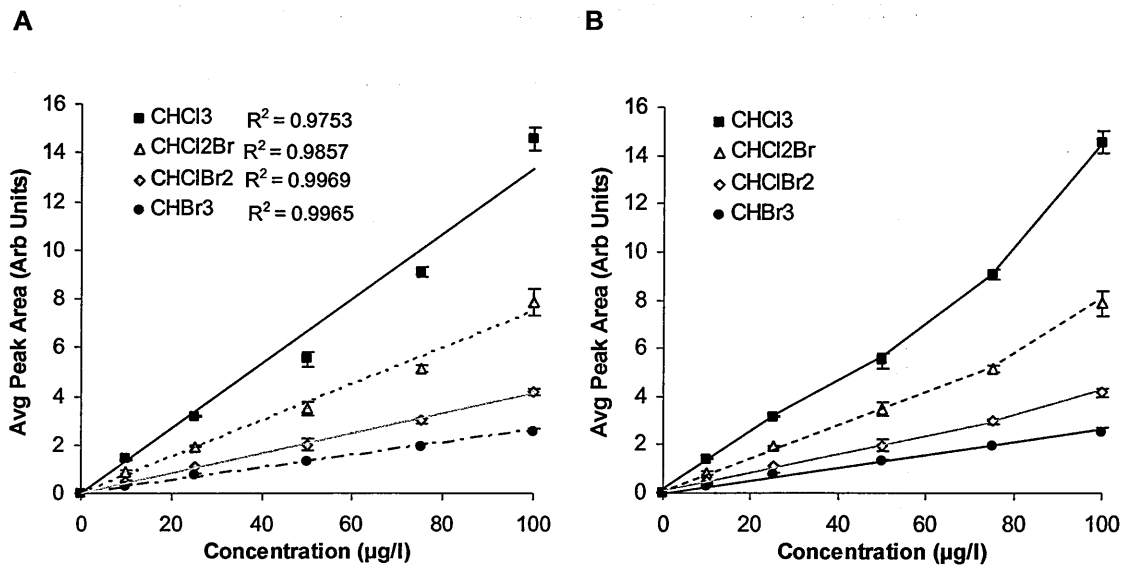


Figure 4.1: A) Six-point calibration curves with linear correlation showing the response of the four THMs standards prepared by the original procedure. B) The calibration curves showing the deviation from linearity. Error bars are standard deviation, σ_{n-1}, from the mean, n=3.

Figure 4.1 are six point calibration curves obtained for each THM at 0, 10, 25, 50, 75 and 100 µg/l. The calibration standards were prepared individually, from an initial stock solution of 100 µg/l, by transferring the required volume of stock solution to a beaker prior to dilution in a volumetric flask. Each concentration was analysed in triplicate by HS-GC-MS using parameters reported in Section 3.1.3.1. The THM calibration curves from this analysis produced poor linear correlation for $CHCl_3$ with a correlation coefficient (R^2) at 0.975. However, the correlation for the other THMs, namely, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ were better (Figure 4.1 A).

As shown in Figure 4.1 B, by placing a line through the points, the deviation from linearity was observed by a clear 'kink', prominent from 75 µg/l to 100 µg/l in the most volatile THM species ($CHCl_3$). A similar but smaller deviation was apparent for $CHCl_2Br$ and $CHClBr_2$. $CHBr_3$ showed no such deviation. It is proposed that this deviation from linearity was probably because of the loss of the more volatile THMs at the transfer stages during dilution.

The issue was resolved by preparing a 5 µg/ml THM stock standard solution in a 4 ml clear glass volumetric flask. The flask was partially filled with ultrapure water and 100 µl of the 200 µg/ml THM calibration mix (Supelco, UK) was injected using a 100 µl glass micro-syringe. The flask was made up to the mark with ultrapure water and shaken gently. For each of the serial dilution of 10, 25, 50, 75 & 100 µg/l, appropriate volumes of ultrapure water were placed in 10 ml glass headspace vials. Owing to the volatile nature of the target species, these vials were cooled to approximately 4 °C in a fridge before the addition of the standards. A volume of the 5 µg/ml THMs stock solution was then injected using 10, 50 and 100 µl glass micro-syringes. The vials were immediately crimp sealed. A blank standard containing just ultrapure water was also prepared by the same method. These standards were then analysed in triplicate by HS-GC-MS. The results are shown in Figure 4.2.

The results of the THM calibration curves obtained from optimised procedure showed linear correlation coefficients (R^2) between 0.992 - 0.999 for all four THMs (Figure 4.2). Most importantly the kink seen previously is no longer present indicating that the hypothesis that the serial dilutions were influencing the yield was valid.

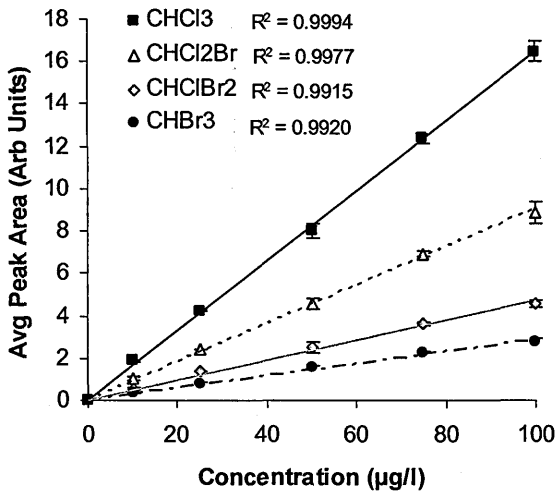


Figure 4.2: Six-point linear calibration curves with linear correlation of the four THMs obtained by HS-GC-MS. Error bars are standard deviation, σ_{n-1}, from the mean, n=3.

These findings demonstrated that the optimised procedure provided better responses and superior linearity, compared to the original procedure. Table 4.1 summarises the deviation based on the relative average peak areas of the procedures.

Table 4.1: The relative peak areas for the optimised procedure normalised to original procedure (n=3).

THMs	100 µg/l	75 µg/l	50 µg/l	25 µg/l
$CHCl_3$	1.13 ± 0.07	1.36 ± 0.03	1.45 ± 0.03	1.33 ± 0.07
$CHCl_2Br$	1.13 ± 0.09	1.35 ± 0.08	1.31 ± 0.03	1.25 ± 0.08
$CHClBr_2$	1.10 ± 0.08	1.22 ± 0.08	1.26 ± 0.03	1.24 ± 0.09
$CHBr_3$	1.08 ± 0.09	1.17 ± 0.07	1.15 ± 0.09	1.04 ± 0.08

As expected from inspecting the graphs, the results obtained at 25, 50 and 75 µg/l showed greatest differences between the two procedures. The yield was also associated with the volatility of the compounds, since $CHCl_3$ showed the greatest difference, whilst $CHBr_3$ showed the least difference, indicating that the volatile species were being preferentially lost in the original method. All THM standards in the experiments reported in this and later chapters were prepared using the optimised procedure.

4.3 Results and discussion

4.3.1 Optimisation of headspace-GC-MS (HS-GC-MS) for the analysis of THMs

4.3.1.1 Setting of the baseline parameters for evaluation

Within the literature there are significant differences in the parameters reported for the analysis of THMs using HS-GC-MS, as summarised in Table 4.2.

Table 4.2: A comparison of the headspace parameters for THMs analysis by static HS.

Parameters	**Values**				
Vial size (ml)	10	20	20	12	12
Water volume (ml)	5	10	10	8	8
Incubation temperature (°C)	60	30	60	45	45
Incubation time (min)	30	30	45	45	40
Agitation	Yes	n/r	n/r	n/r	n/r
Injection volume (µl)	1000	1000	500	n/r	500
Reference	[1]	[2]	[3]	[4]	[5]

References: [1] Toussaint et al. (2001), [2] Duong et al. (2003), [3] Culea et al. (2006), [4] Golfinopoulos et al. (2001), [5] Nikolaou et al. (2002), n/r - not reported.

Owing to the variation of parameters reported within the literature a baseline set-up (derived from literature and discussions with colleagues) was selected to provide a starting point for various optimisations for different headspace parameters. The baseline conditions selected were:

- 10 ml headspace vials, allowing 5 ml of water and 5 ml of headspace;
- headspace syringe was heated to 60 °C;
- vials were incubated for 30 minutes at a temperature of 60 °C; and
- vials were agitated for 4 seconds at 500 rpm and paused for 2 seconds;
- headspace volume injected 500 µl.

The influence of vial size, incubation temperature, incubation times, vial agitation, syringe temperature and quenching salt were all evaluated. The results of these experiments produced the final instrument parameters, which have been reported in Chapter 3.

4.3.1.2 The influence of experimental parameters on the responses of THMs

Vial size

As an integral piece of apparatus, the possible influence of the size of vials used (2, 10 and 20 ml) on the responses obtained for individual THMs was investigated. Triplicate THM standards, at a concentration of 100 µg/l of each THM, were prepared for each of the three vial sizes. The vial phase ratio (β) was maintained at 1 and a constant injection volume of the headspace (500 µl) was used for each.

The ratios of the THMs peak areas for the 20 and 2 ml vials, relative to the peak areas of the 10 ml vial, are summarised in Table 4.3. The ratios demonstrated that for a given phase ratio, in this case 1, the THMs responses in the 20 ml vial gave slightly more yield compared to the 2 ml vials. However, this was not significant and was within the margins of error.

Table 4.3: The ratio of the THMs for the 2 and 20 ml vials relative to the 10 ml vial size (n=3).

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
2 ml	0.92	0.93	0.95	0.94
	± 0.12	± 0.15	± 0.15	± 0.12
20 ml	1.04	1.02	1.07	1.04
	± 0.12	± 0.15	± 0.15	± 0.10

These results confirm the theory that there is no direct correlation between vial size and abundance of analyte in the headspace. For example in headspace sampling (HS) an aliquot of the gaseous phase above the liquid sample is allowed to reach equilibrium for a specific period at a controlled temperature. The phase ratio represents the relative volumes of the two phases in the vial which is determined by the Equation 4.1 (Kolb *et al.*, 1997).

$$\beta = \frac{V_g}{V_s}$$ Equation 4.1

β is the gas sample phase ratio, V_g is the volume of the headspace sample (ml), and V_s is the volume of the liquid sample (ml).

Kolb *et al.*, showed that the distribution of the analyte between the two phases, in equilibrium, was expressed by an equilibrium constant or partition coefficient, K. The partition coefficient was determined by a ratio of the concentration of the analyte in the gas (headspace) and sample, as expressed by the Equation 4.2.

$$K = \frac{C_s}{C_g}$$ Equation 4.2

K is the partition coefficient, C_s is the concentration in liquid sample (µg/l), and C_g is the concentration in headspace (µg/l).

Kolb *et al.*, also showed the relationship between C_0 (original concentration in liquid sample) and the concentration in the gas phase, C_g, was determined by Equation 4.3.

$$C_g = \frac{C_0}{K + \beta}$$ Equation 4.3

C_g is the concentration in gas phase (µg/l), and C_0 is original concentration in liquid sample (µg/l), K is the partition coefficient, and β is the phase ratio.

The theory demonstrates that if the parameters of C_0, K and β are kept constant the yield is also expected to be unchanged (Kolb *et al.*, 1997).

There are also practical implications to consider when selecting the size of vial to be used. A smaller vial size would enable faster equilibrium times and require smaller sampling volumes. However, during the preparation and analysis of THMs standards in the 2 ml vials, several problems were encountered. The small vial size caused water to adhere onto the vial walls or caps, thus preventing a clean extraction of the headspace which could ultimately result in possible damage to the analytical system. It is further noted that an injection of 50 % of headspace (500 µl of 1 ml headspace) can lead to a large internal pressure gradient possibly resulting in a loss of sensitivity.

Collectively, these problems resulted in regular injection errors during the analyses of the 2 ml vials. It was thus determined that the 10 ml vial was the most suitable vial size for the THM analysis.

Incubation temperature

Incubation temperatures ranging between 50 and 80 °C were investigated at 10 °C steps. All samples were heated for a constant period of 30 minutes. Analyses were performed in triplicate, so twenty one samples at a concentration of 50 µg/l were prepared simultaneously in 10 ml vials, with a phase ratio of 1. As anticipated, the findings suggest that the incubation temperature does influence the recovery of THMs, as illustrated in Figure 4.3.

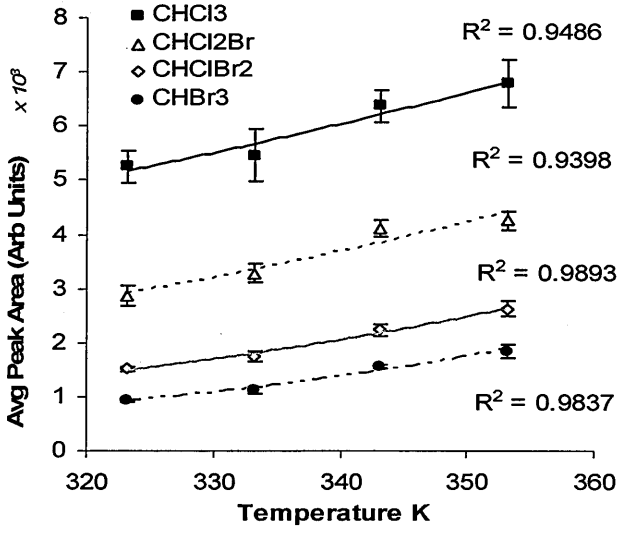


Figure 4.3: The influence of the incubation temperature on the peak areas obtained for the THMs after a constant heating period of 30 min. Error bars are the standard deviation σ_{n-1} from the mean, n=3.

In static headspace extraction, Kolb *et al.* (1997) has reported that the sample incubation temperature and incubation time have an influence on the recovery of the compounds. The incubation temperature has an exponential relationship with the partition coefficient (K) as shown by Equation 4.4 (Kolb *et al.*, 1997).

$$\log K \alpha \frac{1}{T}$$ Equation 4.4

K is the partition coefficient and T is temperature in Kelvins.

Therefore an exponential correlation was introduced, and the results produced coefficients (R^2) between 0.9414 - 0.9824, indicating a possible correlation between temperature and peak areas. An increase in temperature decreases the partition coefficient, hence increasing the proportion of THMs in headspace (C_g). According to Equation 4.3, the influence of headspace would also depend on the relative influence of K and β, but in this case, β was maintained at 1.

The responses from THMs at 80 °C were greater than the responses at lower temperatures. However, in order to prevent the injection of small droplets of evaporated water onto the GC inlet, lower incubation temperatures were generally preferred. A review of the literature showed that the incubation temperature reported in two studies was 45 ° C with a longer heating time of 45 and 40 minutes (Golfinopoulos *et al.*, 2001; Nikolaou *et al.*, 2002b). Other published methods used 60 °C for 45 minutes, 60 °C for 30 minutes and 30 °C for 30 minutes (Culea *et al.*, 2006; Duong *et al.*, 2003; Toussaint *et al.*, 2001). No studies that were investigated reported incubation temperatures greater than 60 °C.

Incubation time

Incubation times of 10, 20 and 30 minutes, at a constant temperature of 60 °C, were investigated. Analyses were performed, in triplicate, as reported above. The influence of heating period (10, 20 and 30 minutes) on the responses of the THMs, at a constant temperature of 60 °C, is shown in Figure 4.4.

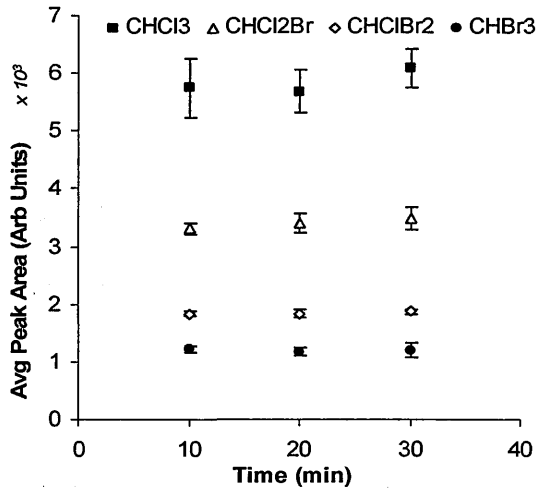


Figure 4.4: The influence of the incubation period on the peak area obtained for the THMs at a constant temperature of 60 °C. Error bars are the standard deviation σ_{n-1} from the mean, n=3.

The findings of this experiment are that the heating periods investigated had a minimal influence on the recovery of THMs. This would indicate that equilibrium has been reached in all cases. The earlier literature review showed that none of the published methods used incubation times below 30 minutes regardless of the other parameters used. In this experiment, although a 10 minute incubation time appears suitable, the settings on the CTC autosampler enabled the sample vials to be heated in parallel to the analyses in GC-MS. Hence, a 30 minute incubation time only adds 20 minutes to the overall cycle time.

Based on the findings of this experiment and a review of literature it was determined that, for a 10 ml vial with a phase ratio of 1, an incubation temperature of 60 °C and heating time of 30 minutes should be used for the analysis of THMs.

Vial Agitation

Twelve analytical standards (50 µg/l of each THM) were prepared. Six standards were analysed using the regular agitation sequence (500 rpm for 4 seconds with a 2 second pause) while the other six standards were analysed without any agitation. The standards were prepared in 10 ml vials with a phase ratio of 1 and were heated at 60 °C for 30

The ratios of the THM peak areas from the agitated and static vials are summarised in Table 4.4. $CHCl_3$ and $CHCl_2Br$ showed a very small increase in response following agitation, but within the margins of error, while $CHClBr_2$ and $CHBr_3$ were not significantly influenced by agitation.

Table 4.4: The ratios of the average peak areas for each of the species after agitation, compared to the peak areas obtained without agitation (n=6).

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
Ratio of peak areas	1.06	1.07	1.01	0.99
	± 0.05	± 0.06	± 0.04	± 0.06

Shaking the vial can assist in achieving equilibrium more quickly by exposing more sample surface area, influencing the time required for the THMs in water and headspace to reach equilibrium *i.e.* increased agitation leads to faster equilibrium. Physical characteristics, such as viscosity, also influence the time required to reach equilibrium (Restek, 2000). The lack of any increase in the response factors was likely to be owing to the incubation time and temperature being sufficient for effective equilibration of the THMs in the headspace and water. A review of literature for headspace GC-MS analyses of THMs showed that, only one study actually reported the use of vial agitation, although others could have shaken the samples vials but did not report it (Culea *et al.*, 2006; Duong *et al.*, 2003; Golfinopoulos *et al.*, 2001; Nikolaou *et al.*, 2002b; Toussaint *et al.*, 2001). However, other headspace (HS) studies of THMs analyses have shown increased THM responses from vial agitation (Kuivinen *et al.*, 1999; Yang *et al.*, 2001). As the capability was available, agitation continued to be used for the THM analyses.

Syringe temperature

Five temperature settings of the headspace syringe were examined, ranging from 30 to 80 °C. Triplicate analyses were performed at each temperature, necessitating the preparation of fifteen replicate standards (100 µg/l of each THM).

A ratio for the average peak areas at the four syringe temperatures, relative to the peak area obtained at 60 °C, were found. The results ranged between 0.97 - 1.07 and are presented in full in Table 4.5. No significant correlation was found between the syringe temperature and the peak area for any of the four THMs, within the margins of error.

Table 4.5: The ratios of the average peak areas for each of the species at various syringe temperatures, relative to those obtained at the baseline temperature of 60 °C (n=3).

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
30 °C	0.97	1.01	1.04	1.01
	± 0.11	± 0.13	± 0.13	± 0.10
50 °C	0.98	1.00	1.01	1.02
	± 0.11	± 0.15	± 0.15	± 0.10
70 °C	0.94	0.97	1.01	1.00
	± 0.11	± 0.15	± 0.14	± 0.13
80 °C	1.01	1.05	1.05	1.07
	± 0.11	± 0.13	± 0.13	± 0.09

A lower syringe temperature might have been expected to show a decrease in THM response because of the formation of cold-spots. However, the results of this experiment showed that syringe temperature did not have any significant influence on the THM responses. Therefore, the initial syringe temperature of 60 °C, similar to the vial temperature, was maintained for the analysis.

Quenching salt

Water samples obtained from treatment works for analyses would generally be quenched with a suitable solution to remove any excess free chlorine and to stop any further chlorination reactions. There are several quenching reagents used in the Water Industry (Worley, 2000). One of the most common quenching reagents used is sodium sulphite (Tikkanen *et al.*, 2001).

Twelve standards were prepared, six with 50 µg/l and another six with 100 µg/l of each THM. Prior to the addition of the stock standard, six standards, at each concentration, were quenched with 5 µl of a sodium sulphite solution (100 µg/ml) to produce a final sodium sulphite concentration of 100 µg/l. The solution of sodium sulphite was obtained from the Cranfield Water Sciences Institute, at Cranfield University, and the concentration value relates to that used in real water samples. The standards were prepared in 10 ml vials with a phase ratio of 1 and were heated at 60 °C for 30 minutes.

A ratio for the average peak areas for the quenched standard, for each of the THM species, for each of the two standards, relative to the unquenched standards, is presented in Table 4.6

Table 4.6: The ratios of the average peak areas for the quenched standard, for each of the THM species, for each of the two standards, relative to the unquenched standards (n=6).

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
50 µg/l	1.01	1.06	1.00	0.98
	± 0.05	± 0.06	± 0.07	± 0.08
100 µg/l	1.04	1.07	1.05	1.03
	± 0.07	± 0.11	± 0.10	± 0.06

The results showed that there was no significant influence as a result of the addition of quenching salt in the response of THMs, within the limits of experimental error.

Kolb *et al.*, (1997) has previous reported that the partition coefficient is inversely proportional to the activity coefficient (γ), as illustrated by Equation 4.5. The activity coefficient describes the intermolecular interaction between analytes and the sample matrix. The addition of salt can alter the sample matrix, which can lead to an increase in the value of K, resulting in greater THMs responses.

$$K \alpha \frac{1}{\gamma}$$ Equation 4.5

K is the partition coefficient γ is the activity coefficient.

Although treated water samples are quenched, the findings in this experiment showed that the addition of salt (sodium sulphite) did not alter the activity coefficient and significantly influence the THM recovery at the expected concentrations used. Hence, the THM calibration standards do not need to be quenched for harmonisation of the experimental procedure between the samples and standards.

A summary of the optimised parameters

Based on experimental results of this study and a review of published studies, the most suitable parameters for the analyses of THMs by HS-GC-MS have been reported in Table 4.7. These parameters have been reported in Chapter 3 and are used for the determination of the linearity, accuracy, precision and limits of detection (LOD) of the HS-GC-MS method.

Table 4.7: The final parameters selected based on the optimisation experiments and literature.

Parameters	**HS-GC-MS analyses**
Headspace vial size (ml)	10
Incubation temperature (°C)	60
Incubation time (minutes)	30
Headspace syringe temperature (°C)	60
Agitation	500 rpm for 4 s with a pause of 2 s
Addition of quenching salt (sodium sulphite)	Not necessary [1]

[1] *The quenching salt at the concentrations used are not necessary in the THM standards for effective harmonisation.*

4.3.1.3 Determination of the linearity, accuracy, precision and limits of detection.

Linearity

The linearity of the HS-GC-MS method was determined by producing a 7-point calibration curve prepared by analysing triplicate calibrations standards containing all the THMs at 0, 5, 10, 25, 50, 75, and 100 µg/l of each species. Good linearity was obtained with correlation coefficients (R^2) higher than 0.9940 for the line of best fit, fitted through least squares (Figure 4.5).

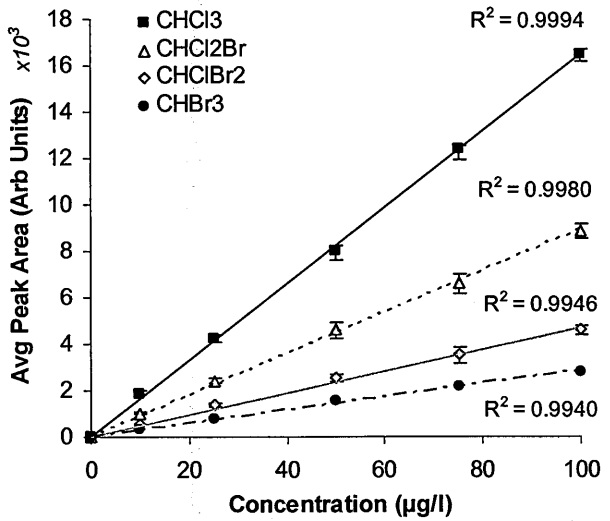


Figure 4.5: The linear calibration plots and the correlation coefficients for the four THMs obtained by HS-GC-MS. Error bars are the standard deviation σ_{n-1} from the mean, n=3.

Accuracy

Accuracy has been defined by the International Organisation of Standards in terms of 'trueness' (ISO 5725-1:1994). It is the exactness of an analytical method, or the closeness of agreement between the value which is accepted either as a conventional, true value or an accepted reference value and the value found. In this case, it is defined as the degree of closeness of a measured concentration to an equivalent point on the calibration curve.

The accuracy was evaluated as follows: Ten replicate THM analytical standards (80 µg/ l of each THM) were prepared and analysed as a batch. THMs standards at 2 µg/l were also investigated (n=10). The concentrations of each THM in the 10 vials were calculated

by use of the 7-point calibration curve. The mean of the replicate concentration measured against the actual concentration (*i.e.* 80 µg/l) provided the accuracy. The HS-GC-MS had an accuracy of between 105.5 and 109.4 % for the higher concentration (80 µg/l) and 104.0 - 115.2 % for the lower concentration (2 µg/l), as summarised in Table 4.9. These levels were within the recommended limits of ± 20 % for analytical measurement (USEPA, 1996a).

Precision

The precision of an analytical procedure expresses the closeness of agreement considered at three levels: repeatability, intermediate precision and reproducibility Repeatability is the variation in results of the method operating over a short time intervals (intra-day), intermediate precision expresses within laboratories variations over different days and while reproducibility expresses the precision between laboratories (Chan *et al.*, 2004).

The repeatability and intermediate precision of the instrument were evaluated as follows: 30 vials of THM standards, at a concentration of 80 µg/l per THM, were prepared simultaneously. These standards were analysed over 3 consecutive days, *i.e.* 10 vials per day. The standard deviation (σ_{n-1}) was calculated for the THMs on the 10 replicate analyses, for each day. The % relative standard deviation against the mean concentration was also calculated.

The repeatability of HS-GC-MS for the THMs was found between 8.22 - 9.18 % for the 80 µg/l and 7.11 - 9.22 % for the 2 µg/l, and intermediate precision was found in the range 7.83 - 9.94 % (Table 4.9). The USEPA reported that a precision of ± 20 % was acceptable for analyses (USEPA, 1996a).

Limits of detection (LOD)

The LODs of each THM were determined as follows: A set of calibration standards and 10 analytical (2 µg/l of each THM) standard vials were analysed. A mean concentration for each THM was calculated, and the standard deviation (σ_{n-1}) of this mean was then determined between the 10 replicates. The LOD was then calculated, using the USEPA Method Detection Limit (MDL) procedure for a Students t value of 99 % confidence level, as illustrated by the Equation 4.6:

$$LOD = \sigma_{n-1} \times 2.821 \qquad \text{Equation 4.6}$$

σ_{n-1} is the standard deviation

2.821 is a Students t value for 99 % confidence level for 10 replicates

Using the above equation, the detection limits for HS-GC-MS were determined as 0.27 - 0.68 µg/l. Table 4.8 compares these LOD values with those reported in the literature for HS-GC-MS. It can be seen that the limits of detection in this study would appear to be higher, than most of the other experiments. This was primarily due the use of an RIC obtained from an ion trap in full scan mode (m/z) will have a much higher LOD, than a quadrupole mass spectrometer used in SIM mode. Alternatively, it may have been because of the method used for the calculation of the detection limits. There were several methods that can be applied for the determination of the detection limits, including graphical s/n ratio and experimental evaluation (Jenke, 2004). One possible explanation is that the other studies may have used graphical s/n ratio to determine the LODs, while this study used a statistically confident experimental method for the determination of the LODs.

Table 4.8: A comparison of the THMs detection limits using static HS-GC-MS.

Compound	LOD (µg/l)						
$CHCl_3$	3	0.1	0.2	0.3	< 0.1	0.003	0.27
$CHCl_2Br$	n/r	0.1	0.05	0.2	< 0.1	0.004	0.48
$CHClBr_2$	n/r	0.1	0.05	0.2	< 0.1	0.007	0.60
$CHBr_3$	3	0.1	0.1	0.2	< 0.1	0.010	0.68
∑THM4		0.4	0.4	0.9		0.024	2.03
Reference	[1]	[2]	[3]	[4]	[5]	[6]	[7]

References: [1] Toussaint et al. (2001), [2] Golfinopoulos et al. (2001), [3] Nikolaou et al. (2002), [4] Duong et al. (2003), [5] Culea et al. (2006), [6] Caro et al. (2007), [7] This work (2008). n/r - not reported.

The measurement of THM4 by HS-GC-MS would have a cumulative error of ± 2.03 µg/l. These error margins were more than adequate for the intended analytical work for the detection and online monitoring of THMs in potable water samples. The detection limits were also more than adequate in the context of the legislation.

A summary of these findings are reported in Table 4.9.

Table 4.9: The mean retention times, linearity correlation coefficient, LOD, accuracy and repeatability of the HS-GC-MS for the analyses of THMs.

Compound	**Mean Retention Time (min)**	**Quantitation ions (m/z)**	**Correlation coefficient** [1] **(R^2)**	**LOD** [2] **(µg/l)**	**Accuracy** [3] **(%)**		**Precision RSD** [4] **(%)**		
							Repeatability (intra-day)	Repeatability (intra-day)	Intermediate precision (inter-day)
				n=10	**2 µg/l** *n=10*	**80 µg/l** *n=10*	**2 µg/l** *n=10*	**80 µg/l** *n=10*	**80 µg/l** *n=30*
$CHCl_3$	1.89	83	0.9994	0.266	104.0	108.3	8.49	8.74	9.94
$CHCl_2Br$	2.72	83	0.9980	0.484	113.7	109.4	9.41	9.18	9.19
$CHClBr_2$	4.01	129	0.9946	0.600	110.2	105.5	6.72	8.22	8.28
$CHBr_3$	5.59	173	0.9940	0.676	115.2	107.7	7.67	8.76	7.83

[1] *The linear range was from 0 - 100 µg/l in triplicates,*

[2] *The LOD was derived from a 2 µg/l THMs analytical standards (n=10),*

[3] *The accuracy of 2 µg/l (n=10) and 80 µg/l (n=10) THMs analytical standards,*

[4] *The precision of 2 µg/l (n=10) and 80 µg/l (n=10, 30) THMs analytical standards.*

4.3.2 Headspace-solid phase micro extraction of THMs by GC-MS (HS-SPME-GC-MS)

As reported in Chapter 1, there are several publications that utilised HS-SPME-GC-MS for the analysis of THMs. Cho *et al.* (2003) and San Juan *et al.* (2007) have optimised several SPME conditions such as fibre type and the influence of acids and salts on the response of THMs. Therefore, this work did not repeat the optimisations already performed.

The selection of the SPME fibre and other desorption conditions were obtained from Cho *et al.* (2003). Experiments to measure the LOD, linearity, accuracy and repeatability of the method were, however, performed and reported here. The procedures used have been described in Section 4.3.1.3, with a few minor variations. The linearity evaluation was performed using 11 THM calibrations standards, in duplicate, at concentrations of 0, 0.1, 0.5, 1, 2, 5, 10, 25, 50, 75 and 100 µg/l. The LOD experiments in this study used standards with a concentration of 0.5 µg/l, while the analytical standards for accuracy and precision measurements had a concentration of 50 µg/l.

A typical total ion chromatogram of the THM standard, at 50 µg/l, obtained by HS-SPME-GC-MS, is given in Figure 4.6 A. The superimposed partially reconstructed ion (RIC) chromatogram of the same standard is also presented in Figure 4.6 B. The chromatograms illustrate good peak shape and chromatographic resolution. Although some peak tailing was observed for the THMs, believed to be because of the desorption profile of CAR-PDMS SPME fibre in the GC-inlet liner, this was deemed acceptable for analytical quantitation. Similar tailing was observed in another HS-SPME method for THMs reported in the literature (SanJuan *et al.*, 2007).

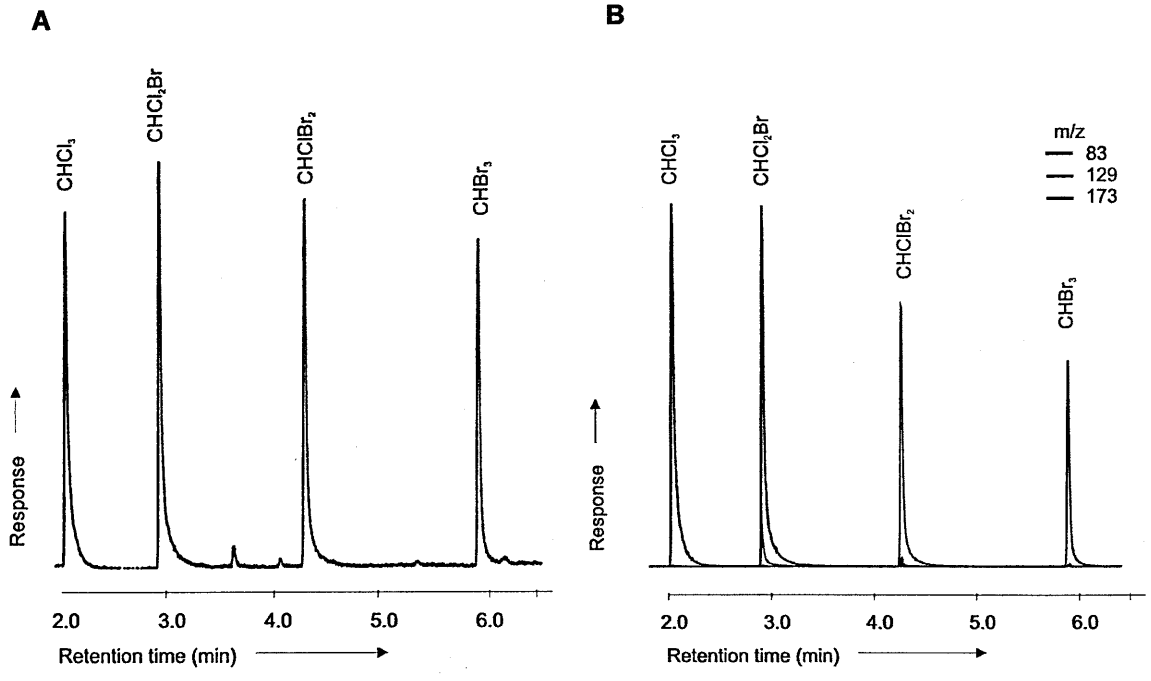


Figure 4.6: A) A total ion chromatogram displaying the four THMs of a 50µg/l. calibration standard obtained by the HS-SPME-GC-MS. B) Superimposed partially reconstructed ion chromatograms (m/z 83, 129 and 173) displaying the four THMs. Not drawn on the same scale.

In contrast to direct headspace analysis, the magnitude of the response using SPME in the total ion chromatogram had the following order: $CHCl_2Br > CHClBr_2 > CHCl_3 > CHBr_3$. Previously the order of response was $CHCl_3 > CHCl_2Br > CHClBr_2 > CHBr_3$. This was probably because of interaction of the THMs on the SPME fibre, allowing preferential adsorption and desorption for some of the THMs, such as $CHCl_2Br$. Similar responses can also be observed in the results by SanJuan *et al.* (2007).

The linearity experiments produced correlation coefficients (R^2) better than 0.9926 for the THMs, as shown by the calibration plots in Figure 4.7.

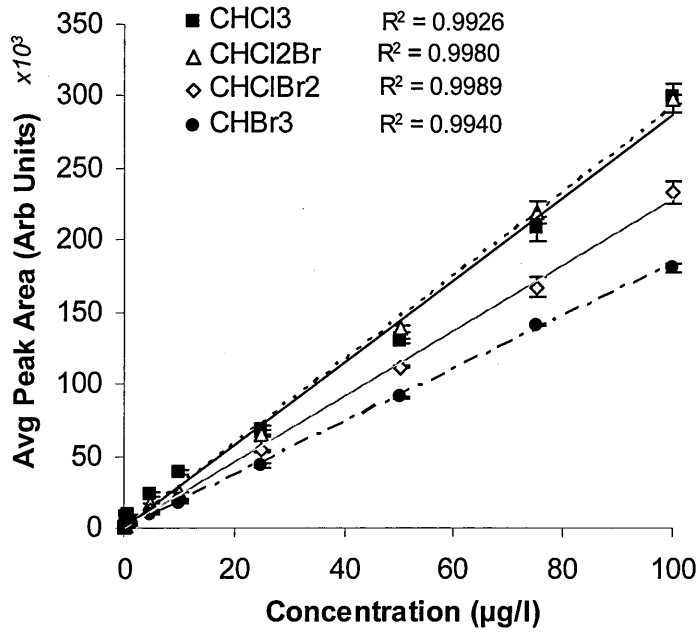


Figure 4.7: The linear calibration plots and the correlation coefficients for the four THMs obtained by HS-SPME-GC-MS.

The detection limits of THMs using HS-SPME-GC-MS was < 0.19 µg/l (Table 4.10). The LODs were compared to other similar studies using HS-SPME-GC-MS found in the literature and are reported in Table 4.10. The detection limits in this study were higher compared to Cho *et al.* (2003) and San Juan *et al.* (2007), but lower than the results reported by Stack *et al.* (2000). However, the former references used a graphical s/n ratio of 3, at low concentrations, to determine the LODs, while the latter reference used a method similar to this study (experimental evaluation) to determine the LOD for the THMs.

Table 4.10: An comparison of the THM LODs using HS-SPME-GC-MS with similar studies reported in literature.

Compound	**LOD (µg/l)**			
$CHCl_3$	2.8	0.010	0.073	0.107
$CHCl_2Br$	1.4	0.005	0.058	0.178
$CHClBr_2$	1.0	0.005	0.018	0.193
$CHBr_3$	1.2	0.010	0.009	0.182
∑THM4	6.4	0.03	0.158	0.660
Reference	[1]	[2]	[3]	[4]

References: [1] Stack et al., (2000), [2] Cho et al., (2003), [3] San Juan et al., (2007), [4] This study, (2008).

As summarised in Table 4.11, the analyses of the THMs in HS-SPME-GC-MS had an accuracy of between 95.9 - 100.4 % for the 50 µg/l standards, while the 0.5 µg/l standards had an accuracy of 98.8 - 109.5 %. The combined intra-day precision (repeatability) ranged from 4.5 - 6.6 % and the inter-day precision ranged from 3.4 - 6.3 %. The repeatability of the 0.5 µg/l was found in the range 3.8 - 6.8 %. The accuracy and precision found here were well within the USEPA recommendation of ± 20 % for analytical methods (USEPA, 1995c)

Table 4.11: The mean retention times, linearity correlation coefficients, LOD, accuracy and precision for the analyses of THMs using the HS-SPME-GC-MS method.

Compound	Mean retention time (min)	Quantitation ions (m/z)	Correlation coefficient [1] (R^2)	LOD [2] (µg/l)	Accuracy [3] (%)		Precision RSD [4] (%)		
							Repeatability (intra-day)	Repeatability (intra-day)	Intermediate precision (inter-day)
				n=10	**0.5 µg/l** *n=10*	**50 µg/l** *n=10*	**0.5 µg/l** *n=10*	**50 µg/l** *n=10*	**50 µg/l** *n=30*
$CHCl_3$	1.88	83	0.9926	0.107	106.9	95.9	3.78	6.41	6.34
$CHCl_2Br$	2.70	83	0.9980	0.178	109.5	96.9	6.30	6.57	5.49
$CHClBr_2$	4.01	129	0.9989	0.193	98.8	99.3	6.83	5.92	4.22
$CHBr_3$	5.60	173	0.9940	0.182	99.0	100.4	6.46	4.53	3.40

[1] *The linear range was from 0 - 100 µg/l in duplicate,*

[2] *The LOD was derived from 0.5 µg/l THMs analytical standards (n=10),*

[3] *The accuracy of 0.5 µg/l (n=10) and 50 µg/l (n=10) THMs analytical standards,*

[4] *The precision of 0.5 µg/l (n=10) and 50 µg/l (n=10, 30) THMs analytical standards.*

4.3.3 Headspace sampling of THMs by GC-μECD (HS-GC-μECD)

Experiments to determine the linearity, repeatability, accuracy and LOD of HS-GC-μECD used procedures similar to those described in Section 4.3.2.7 and the instrument parameters used have been reported in Chapter 3. The evaluation of linearity was performed on triplicate injections of seven calibration standards at 0, 0.1, 10, 25, 50, 75 and 100 μg/l, respectively. The repeatability and accuracy was determined by analysing ten standards at concentrations of 50 μg/l and 0.1 μg/l. The LOD for each THM were determined by the analysis of ten THM analytical standards at a concentration of 0.1 μg/l.

The calibration curves obtained from HS-GC-μECD showed excellent linearity with correlation coefficient better than 0.9979, as shown by Figure 4.8.

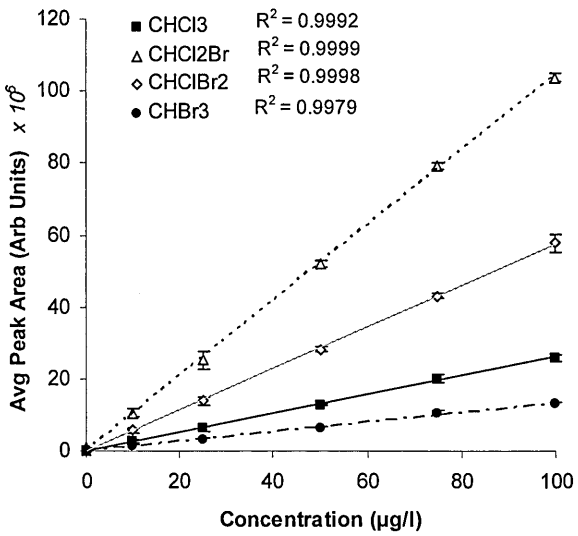


Figure 4.8: The linear calibration plots and the correlation coefficients for the four THMs obtained by HS-GC-μECD.

Table 4.12 shows that the accuracy determined for each THM was between 93.0 - 101.2 % and 83.0 - 90.8 % for the 50 μg/l and 0.1 μg/l standards, respectively. The repeatability of measuring each THM was 3.5 - 8.1 % for the 50 μg/l standard and 7.6 - 13.4 % for the 0.1 μg/l standard. As anticipated, at lower concentrations, repeatability and accuracy were worse than at higher concentrations. The detection limits for the THMs were between 0.02 - 0.03 μg/l using the HS-GC-μECD.

Table 4.12: The mean retention times, linearity correlation coefficients, LOD, accuracy, and repeatability for the analyses of THMs using HS-GC-μECD.

Compound	Mean retention time (min)	Correlation coefficient [1] (R^2)	LOD [2] (μg/l)	Accuracy [3] (%)		Repeatability RSD [4] (%)	
				0.1 μg/l	50 μg/l	0.1 μg/l	50 μg/l
			n=10	*n=10*	*n=10*	*n=10*	*n=10*
$CHCl_3$	1.87	0.9992	0.028	86.9	93.0	11.11	8.14
$CHCl_2Br$	2.69	0.9999	0.022	90.8	101.2	11.40	5.83
$CHClBr_2$	4.00	0.9998	0.015	83.0	97.9	7.55	3.64
$CHBr_3$	5.58	0.9979	0.031	86.6	98.8	13.04	3.45

[1] *The linear range was determined from 0 - 100 μg/l,*

[2] *The LOD was derived from 0.1 μg/l THM analytical standards (n=10),*

[3] *The accuracy of 0.1 μg/l (n=10) and 50 μg/l (n=10) THM analytical standards,*

[4] *The repeatability of a 0.1 μg/l (n=10) and 50 μg/l (n=10) THM analytical standards.*

4.3.4 Liquid-liquid extraction of THMs by GC-μECD (LLE-GC-μECD)

Several LLE-GC-μECD methods have been reported in the literature for the measurement of THMs, including USEPA Method 551 and Method 551.1, as summarised in Chapter 1. LLE-GC-μECD was evaluated to provide a baseline performance for THM concentration measurement. All the sample preparation and extraction was performed by members of Cranfield Water Science Institute, while the concentration measurements were performed at The Open University.

The instrument parameters used have been reported in Section 3.1.3.4. The details of the liquid-liquid extraction procedures are described in Appendix 2. Experiments to measure linearity, accuracy, repeatability and detection limits were performed on the GC-μECD using procedures similar to those described in Section 4.3.2.7. The linearity evaluation was performed by single injections of calibration standards at 0, 1, 10, 25, 50 and 100 μg/l, respectively. The repeatability and accuracy was measured by the same day analysis of seven THM standards, at a concentration of 50 μg/l, for each THM. A single point internal standard method was used for the quantitation of THMs. The LOD, in this case, was performed on analyses of seven standards (1 μg/l of each THM). The internal standard, bromofluorobenzene, at a concentration of 1000 μg/l was selected based on USEPA Method 551.1 (1998).

The results shown in Table 4.13 illustrates that the method had linearity, for each THM, with R^2 better than 0.9933. The repeatability was between 1.3 and 3.4 % for each of the species, with an accuracy of 93.8 - 96.9 %. Good detection limits, below 0.06 μg/l, were also observed.

Table 4.13: The mean retention times, linearity correlation coefficients, LOD, accuracy and repeatability of THMs using the LLE-GC-μECD.

Compound	Mean retention time (min)	Correlation coefficient [1] (R^2)	LOD [2] (μg/l)	Accuracy [3] (%)	Repeatability RSD [4] (%)
$CHCl_3$	3.30	0.9933	0.056	93.8	3.39
$CHCl_2Br$	4.69	0.9961	0.013	94.0	1.50
$CHClBr_2$	6.87	0.9979	0.018	95.7	1.26
$CHBr_3$	9.57	0.9992	0.015	96.9	1.34

[1] *The linear range was from 1 - 100 μg/l,*

[2] *The LOD was derived from a standard of 1 μg/l (n=7),*

[3] *The accuracy of a 50 μg/l THM analytical standard (n=7),*

[4] *The repeatability of a 50 μg/l THM analytical standard (n=7).*

4.3.5 Application of HS-GC-MS, HS-SPME-GC-MS and HS-GC-μECD to the analysis of THMs in treated water samples

The opportunity was taken to conduct a comparative study to evaluate the relative performances of HS-GC-MS, HS-SPME-GC-MS and HS-GC-μECD on the same treated water samples. LLE-GC-μECD was not evaluated because the ultimate aim of this research was to explore analytical methods for potential near-real time analysis of THMs. The sample was provided by Cranfield Water Science Institute, was a NOM fraction of treated lowland water that had been chlorinated in the laboratory for seven days.

The analytical parameters used in this study were those reported in Chapter 3. Samples were analysed in triplicate on each instrument. The THM detection limits, based on the analyses of calibration standards in purified water, of the three methods has been reported earlier in Tables 4.9, 4.10 and 4.13. Good linear correlations coefficients were

obtained for the three methods for all four THMs (> 0.9962). The individual and mean THM4 concentrations obtained by each method has been summarised in Table 4.14.

Table 4.14: Comparison of the THM concentrations between the three methods (n=3).

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	THM4
HS-GC-MS	10.85 ± 0.70	34.70 ± 0.48	56.91 ± 2.10	27.64 ± 0.43	130.09 ± 2.31
HS-SPME-GC-MS	11.04 ± 1.21	32.35 ± 1.90	58.10 ± 5.08	28.64 ± 0.62	130.13 ± 5.59
HS-GC-μECD	11.75 ± 0.08	37.05 ± 1.94	59.08 ± 0.98	30.46 ± 1.19	138.33 ± 3.36

Error bars are the standard deviation σ_{n-1} *from the mean, n=3.*

The correlation between HS-GC-MS and HS-SPME-GC-MS was close, with a deviation of 1.7 - 6.9 % for each of four THMs species and < 0.5 % for the mean total THM4 concentration between the two instruments. The THM concentrations were slightly higher on the HS-GC-μECD compared to HS-GC-MS, with the mean THM4 concentration being 1.06 times higher with variances of 1.7 - 13.5 % for the individual THM species. In both cases, $CHCl_2Br$ was responsible for the greatest deviations, however, it accounted for the highest concentrations.

The degree of agreement between the THM measurements is illustrated in Figure 4.9. A line of equality, which illustrates a value if the two instruments gave the same reading, is drawn. This visually indicates a close correlation between HS-GC-MS and HS-SPME-GC-MS and the slightly higher correlation for the HS-GC-μECD for all four THMs.

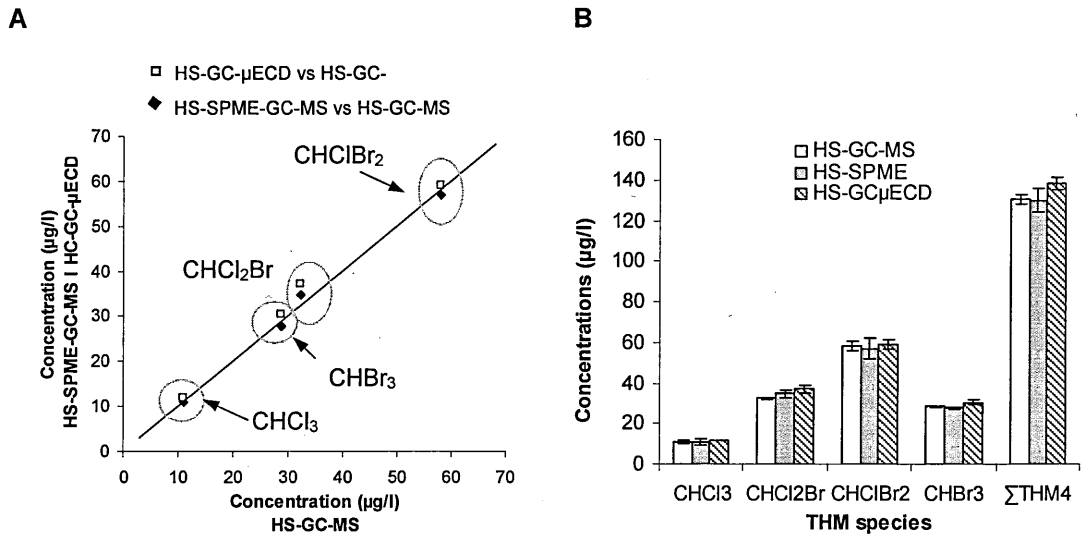


Figure 4.9: A) A graph showing the THM concentrations for each of the three methods. The line of equality has been drawn through the plot does not represent the best fit line. B) The individual and THM4 concentrations for each of the three methods. Error bars for THM4 are cumulative error of the sum of the mean concentrations, n=3.

Although the results from HS-GC-µECD were slightly higher, these results were still within acceptable deviations (< 20 %) (DWI, 2008). In summary, all three methods were found to be analytically comparable. Hence other practical considerations can to be looked at, for the selection and use, specifically for the intended purposes of near-real time analyses of THM for monitoring purposes.

4.4 Discussion of the methods investigated

In the UK, regulations state that the total THM concentration should not exceed 100 µg/l (DWI, 2010c).This chapter has investigated the analytical performance of four different methods for the analysis of THMs. The techniques (HS-GC-MS and HS-SPME-GC-MS) have been selected based on their potential to be applied for the near-real time monitoring of THMs. The performance of these methods (linearity, accuracy, reproducibility and LOD) were evaluated against the performance of existing methods, which show less potential for near-real time monitoring (HS-GC-µECD and LLE-GC-µECD). Table 4.15 compares the results obtained for each system and those previously reported for USEPA Method 501.3 (1996).

Table 4.15: Overview of the sample preparation, instrument analysis times, linearity, repeatability, accuracies and LODs of methods investigated for the analysis of THMs in this study, compared to the USEPA Methods 501.3, 524.2 and 551.1.

Instrument	Sample Preparation	Analysis Time (minutes)	Linearity (R^2)	Precision (%)	Accuracy (%)	LOD (µg/l)
HS-GC-MS	Minimum Sample Preparation	< 10	0.9940 - 0.9994	8.2 - 9.2 (80 µg/l) [1] 6.7 - 9.4 (2 µg/l) [1] 7.8 - 9.9 (80 µg/l) [2]	105.5 - 109.4 (80 µg/l) 104.0 - 115.2 (2 µg/l)	0.27 - 0.68 THM4 < 2.03
HS-SPME-GC-MS	Minimum Sample Preparation	< 10	0.9926 - 0.9980	4.5 - 6.6 (50 µg/l) [1] 3.8 - 6.8 (0.5 µg/l) [1] 3.4 - 6.3 (50 µg/l) [2]	95.9 - 100.4 (50 µg/l) 98.8 - 109.5 (0.5 µg/l)	0.11 - 0.19 THM4 < 0.70
HS-GC-ECD	Minimum Sample Preparation	< 10	0.9979 - 0.9999	3.5 - 8.1 (50 µg/l) [1] 7.6 - 13.4 (0.1 µg/l) [1]	93.0 - 101.2 (50 µg/l) 83.0 - 90.8 (0.1 µg/l)	0.02 - 0.02 THM4 < 0.10
LLE-GC-µECD	Sample preparation required ~ 1 hour	< 15	0.9933 – 0.9992	1.26 - 3.39 (50 µg/l) [1]	93.8 - 96.9 (50 µg/l)	0.02 - 0.06 THM4 < 0.10
USEPA 501.3 (1996) PT-GC-MS (SIM)	Minimum Sample Preparation	n/r	n/r	2.8 - 10.2 (0.2 µg/l) [1]	90.8 - 106.0 (0.2 µg/l)	0.06 - 0.07 THM4 < 0.10
USEPA 524.2 (1995a) PT-GC-MS	Minimum Sample Preparation	< 28	n/r	6.1 - 6.4 % (0.1 µg/l)	90.0 - 101.0 (2-5 µg/l)	0.03 - 0.12 THM4 < 0.28
USEPA 551 (1990a) LLE-GC-ECD	Sample preparation required ~ 1 hour	< 32	n/r	0.7 - 2.7 (0.2 - 2.0 µg/l)	80 - 109 (0.2 - 2.0 µg/l)	0.002 - 0.012 THM4 < 0.032
USEPA 551.1 (1995b) LLE-GC-ECD	Sample preparation required ~ 1 hour	< 30	n/r	2.8 - 4.1 (5.0 µg/l)	85 - 101 (5.0 µg/l)	0.01 - 0.08 THM4 < 0.18
USEPA 501.3 Recommendation	n/a	n/r	n/a	< 15 %	100 ± 10 %	n/a

[1] Repeatability – precision measured by running standard on the same day (Intra-day Precision); [2] Intra-day Precision – precision measured by running standards on three different days (Inter-day Precision). n/r - not reported, n/a - not applicable.

Both HS-GC-MS and HS-SPME-GC-MS have good linearity, repeatability and accuracy, and are within the levels required by DWI and USEPA Methods. In addition, the analysis times for both techniques are sufficiently short and require minimal sample preparation.

A closer examination of the detection limits for the THMs from the four methods utilised in this study, as well as the established USEPA Methods 501.3 and USEPA Methods 524.2 (PT-GC-MS) and 551.1 (LLE-GC-μECD), has been summarised in Table 4.16. The HS-GC-μECD and LLE-GC-μECD were the most sensitive, with similar detection limits to the established USEPA methods. The HS-GC-MS and HS-SPME-GC-MS had higher detection limits.

Table 4.16: A comparison of the limits of detection for each THM by each analytical method.

Compound	**LOD (μg/l)**						
	HS-GC-MS [1]	HS-SPME-GC-MS [1]	HS-GC-μECD [1]	LLE-GC-μECD [1]	PT-GC-MS [2]	LLE-GC-ECD [3]	PT-GC-MS [4]
$CHCl_3$	0.27	0.11	0.03	0.06	0.03	0.08	0.06
$CHCl_2Br$	0.48	0.18	0.02	0.01	0.08	0.07	0.07
$CHClBr_2$	0.60	0.19	0.02	0.02	0.05	0.01	0.05
$CHBr_3$	0.67	0.18	0.03	0.01	0.12	0.02	0.04
∑THM4	2.03	0.70	0.10	0.10	0.28	0.18	0.10

References: [1] This research, [2] USEPA 524.2 (1995 a), [3] USEPA 551.1 (1995 b) and USEPA 501.3 (1996)

Whilst the detection limits for HS-GC-MS and HS-SPME-GC-MS were higher, than those reported in the USEPA Methods, or by HS-GC-μECD and LLE-GC-μECD, they are sufficiently low to be useful for monitoring purposes, particularly in the context of the regulatory requirements for THM4 concentration of 100 μg/l. Of greater importance in the context of sample monitoring is the linearity, repeatability and accuracy of the method. It should also be noted that the requirements of a monitoring system would differ from those require from regulatory compliance, particularly in the context of real and near real-time analysis, as illustrated in Table 4.17.

Table 4.17: Comparison of the requirement of continuous monitoring with the regulatory compliance.

Criterion	Continuous monitoring	Regulatory compliance
Location	Water Treatment and Distribution system	Regulatory Laboratory
Responses	Alarm or level indicators	Regulatory compliance protocols
Analyses type	Real time (online) or near real time (off line)	Retrospective analyses (up to 2 weeks)
Frequency	Company policy (such as 1 sample a day)	Regulatory compliance (such as two samples every month)
Maintenance	Easy maintenance	Standard laboratory procedures of maintenance
Operator Skill	Semi skilled operators	High skilled operators
Cost	Cheaper and smaller	High end apparatus

In addition to the analytical performance, other criteria need to be considered to evaluate the relative merits of each method. Table 4.18 attempts to provide such a comparison.

Table 4.18: A general comparison of the methods for the measurement of the THMs.

Performance Criterion	HS-GC-MS	HS-SPME-GC-MS	HS-GC-μECD	LLE GC-μECD
Sensitivity	Low sensitivity (~1)	Higher sensitivity (~8x)	Higher sensitivity (~22x)	Higher sensitivity (~20x)
Linearity, repeatability and accuracy	Comparable	Comparable	Comparable	Comparable
Analytical Speed	Comparable	Comparable	Comparable	Comparable
Operation skills	Minimum complexity	Increased complexity owing to the use of a fibre	Minimum complexity	Increased complexity owing to the requirement for additional solvents
Contamination	Minimum contamination and low carryover because of the system purge with pure Helium	Increased possibility of contamination from fibres adsorption with increased possibly of carryover	Minimum contamination and low carryover because of the system purge with pure Helium	Increased possibility of contamination from solvents during extraction
Sample preparation	Minimum sample preparation	Minimum sample preparation	Minimum sample preparation	Increased sample preparation requiring solvents
Regulations	n/a	n/a	Requirement to have a permit for the μECD	Requirement to have a permit for the μECD
Automation	Can be easily automated (CTC MPS 2)	Can be easily automated (CTC MPS 2)	Can be easily automated (CTC MPS 2)	Potentially harder to automate (MLLE?)
Consumable costs	Minimum costs	Higher costs due to SPME fibres	Minimum costs	Costs of handling and disposal of solvents
Capital costs	Higher because of the cost of MS. May become lower as deployable systems become available	Higher because of the cost of MS. May become lower as deployable systems become available	Lowest cost	Lower analytical instrument cost but may require solvent handling equipment

4.5 Conclusions and future work

In conclusion, this chapter has optimised existing analytical methods that would be suitable for translation to near real-time monitoring of THM concentrations. The performances of HS-GC-MS, HS-SPME-GC-MS and HS-GC-μECD were all evaluated in terms of their linearity, repeatability, accuracy and LODs, against published methods (LLE-GC-μECD).

This study has shown that THMs can be detected and quantified using several different methods with suitable levels of analytical performance to enable near-real time analysis. HS-GC-MS and HS-SPME-GC-MS are both believed to be viable for such a monitoring system, if an affordable GC-MS system becomes available.

Before any such system could be implemented, further work would be required to comply with the provisions required by the DWI for the online monitoring (DWI, 2010b). These would include:

- the requirement that the results are representative of the water being supplied;
- the system is maintained and operated to a demonstrably high standard at all times;
- the system is calibrated in a way that is valid, appropriate and traceable;
- the system is subject to reliable quality checks at an appropriate frequency; and
- the recorded reading is the true reading of the instrument at that time.

5. The development and optimisation of methods for the analysis of haloacetic acids (HAAs)

5.1 Introduction

There are nine commonly-occurring chlorinated and brominated haloacetic acids (HAAs), five of which have been regulated in the United States at a total concentration of 60 µg/l (USEPA, 1998b). HAAs are currently not regulated in the United Kingdom and the European Union (EU). However they are considered as high priority compounds for potential regulation in the near future (Fawell *et al.*, 2002), and are listed for future regulation in the EU Water Directive (Cortvriend, 2008). In order to prepare for this regulation, water companies are taking a proactive approach to assess the most appropriate methodology for the analysis of HAAs in their water samples.

As described in Chapter 1, there are several analytical methods reported in the literature for the analysis of HAAs, such as: GC-µECD, GC-MS, HPLC, CE and IC. Most of the USEPA Methods are based on the use of GC-µECD, owing to the detector's high response to the electronegative halogens. Currently four USEPA approved methods use the GC-µECD: USEPA Method 552.1 (1992), USEPA Method 552.2 (1995), USEPA Method 552.3 (2003) and Standard Method 6251 (APHA, 1998). Although GC methods involve labour intensive and time consuming sample extraction processes and use of toxic derivatisation reagents, they are highly sensitive, accurate and reliable. Other methods such as HPLC, CE and IC are faster with minimal sample preparation; however, they have significantly higher detection limits (Carrero *et al.*, 1999).

Whist GC-µECD is the most frequently used technique for the analysis of HAAs, it is not without its issues. Some of the draw-backs for the analysis of HAAs using a GC-µECD include:

- the requirement of having a permit for using a radioactive ^{63}Ni source, which is present in the detector and can be limiting if required beyond a standard analytical laboratory (Agilent, 2007b; HSE, 1999);
- the low sensitivity of some HAA such as MCAA (Nikolaou *et al.*, 2002a; Xie, 2001);
- an inability to measure some HAAs such as MCAA (Malliarou *et al.*, 2005; Reckhow *et al.*, 2008; Xie, 2001);
- chromatographic interference (Xie, 2001) which can lead to the possibility of co-elution of compounds with the HAAs;
- complexity of sample preparation and the use of hazardous derivatisation reagents (Nikolaou *et al,* 2002).

The aim of this work was to investigate whether alternative chromatographic methods were as suitable for the analysis of HAAs. The analytical instruments investigated were: GC-μECD, GC-MS (in electron impact ionisation mode), GC-MS (in chemical ionisation mode) and comprehensive chromatography (GC×GC-ToFMS). Comprehensive, or two-dimensional, gas chromatography (GC×GC) is the serial coupling of two GC columns (of different polarity) interfaced with a thermal modulator where compounds from the first column are continuously trapped and re-focused into the second column as discrete fractions. The research also investigated the influence of instrument parameters on the performance of the analyses. These were primarily performed on GC-μECD. Parallel research, at Cranfield University, explored the use of Ion Chromatography (IC) for the analyses of HAAs.

Ultimately, the optimised methods were to be used for evaluation of the formation potentials of the individual HAAs in Chapter 6 and a study of the HAA concentrations present in water samples from around the UK, as reported in Chapter 7. At the time this work was conducted, only one such study had been reported in the literature for UK (Malliarou *et al.*, 2005).

5.2 Materials and methods

Two separate HAA standards were used during this investigation: a HAA6 calibration mix (2000 µg/l per HAA, Supelco UK) containing the five US regulated HAAs and the unregulated BCAA; a HAA9 calibration mix (2000 µg/l per HAA, Supelco UK) that contained all nine of the commonly occurring HAAs.

As reported in Chapter 3, before analysis both standards had to be derivatised, so as to convert the HAAs to their methyl esters, resulting in solutions that were more GC amenable. All the sampling, preparation, extraction and derivatisation was performed by members of the Cranfield Water Science Institute, Cranfield University. The derivatised method used in this study has been reported by Bougeard (2009) and is a modified version of USEPA Method 552.2 (1995) developed by Tung and colleagues (Tung *et al.*, 2006). A schematic of this method is provided in Appendix 3. As a consequence of derivatisation there is the possibility that HAAs can be lost. However, whenever the concentrations of HAAs are quoted within this Chapter, a derivatisation efficiency of 100 % has been assumed. The concentration values reported for the HAA standards represent the concentration for each HAA present in the standard. The compound 1,2,3-trichloropropane was used as the internal standard at a concentration of 1,000 µg/l.

The optimisation of the chromatographic and instrument parameters were performed by the author at The Open University. The final instrumental conditions, the materials and experimental parameters have been reported in full in Chapter 3.

5.3 Results and discussion of the analytical experiments

5.3.1 The analysis of HAAs using Ion Chromatography

Colleagues at Cranfield University investigated the use of IC for the analysis of HAAs, as it potentially offered a cheaper and faster (< 10 min) alternative to the preparation methods required for GC analysis. However, Bougeard (2009) reported that the limits of

detection (LOD) for the nine HAAs were very poor (2.6 - 31.9 µg/l) and were believed to be as a result of matrix impact. As these levels were higher than their required criteria of 0.17 µg/l of each HAA, they concluded that the method was not suitable for the measurement of HAAs in UK treated waters. Liu and Mou (2003) have also reported high detection limits for HAA9 at 0.4 -31.9 µg/l, whilst Nair and colleagues reported LODs for HAA6 at 8 - 80 µg/l. Recommended Minimum Reporting Levels (MRL), as required by USEPA DBP/ICR Analytical Methods Manual (1996) for each of the nine HAAs, range from 1 - 4 µg/l. Hence, no further work was undertaken on this instrument.

5.3.2 The analysis of HAAs using GC-µECD

Given the large variability in the instrumental parameters reported in literature for the analysis of HAAs, and having learnt lessons from the analysis of THMs, it was decided to investigate the influence of various instrument parameters on the response for the individual HAAs. Parameters such as: the choice of the GC-capillary column stationary phase, the oven temperature program, and the inlet and detector parameters were studied. Once optimised, experiments to measure the LOD, precision and accuracy of the instrument were also performed.

5.3.2.1 The influence of the GC capillary columns on the response of HAAs in the GC-µECD

Prior to the study, a brief review of the literature was performed to evaluate the common stationary phases used for HAA analyses by GC-µECD, as reported in Table 5.1. Xie (2001), whose sample extraction methods were modified for use in this research, used a HP 5MS (95 % dimethyl, 5 % diphenyl polysiloxane) column for the analyses of the HAAs on a GC-MS.

Table 5.1: Various columns used in the analyses of HAAs with GC-μECD reported in literature.

Column name	Column dimensions	HAAs	Reference
J&W DB 5.625 (P)	30 m × 0.25 mm id × 0.25 μm	HAA9	(USEPA, 1995b)
J&W DB 5.625 (C)	30 m × 0.25 mm id × 0.25 μm	HAA9	(USEPA, 2003a)
J&W DB 1701 (C)	30 m × 0.25 mm id × 0.25 μm	HAA9	(USEPA, 1995b)
J&W DB 1701 (P)	30 m × 0.25 mm id × 0.25 μm	HAA9	(USEPA, 2003a)
J&W DB 1	30 m × 0.32 mm id × 0.25 μm	HAA9	(Nikolaou *et al.*, 2002a)
J&W DB 1	30 m × 0.25 mm id × 1.0 μm	HAA9	(Villanueva *et al.*, 2003)
J&W DB 1	30 m × 0.32 mm id × 1.8 μm	HAA9	(Nikolaou *et al.*, 2004b)
J&W DB 1701	30 m × 0.25 mm id × 0.25 μm	HAA6	(Pepich *et al.*, 2004)
J&W DB 5MS	30 m × 0.25 mm id × 0.25 μm	HAA9	(Qi *et al.*, 2004)
J&W DB 5MS	30 m × 0.25 mm id × 0.25 μm	HAA9	(Yang *et al.*, 2005)
ZB-1701	30 m × 0.32 mm id	HAA6	(Rodriguez *et al.*, 2007)
J&W DB 1	30 m × 0.32 mm id × 1.0 μm	HAA5	(Uyak *et al.*, 2007a)
Agilent HP-5	30 m × 0.32 mm id × 0.25 μm	HAA5	(Li *et al.*, 2008)

(P) as primary and (C) as confirmation.

The USEPA method 552.2 (1995) reported the use of the J&W DB-5.625 column (95 % dimethyl, 5 % diphenyl polysiloxane) as the primary column and the mid polar J&W DB-1701 column (14 % cyanopropylphenyl, 86 % dimethyl polysiloxane) as the confirmation column. The USEPA Method 552.3 (2003) used a mid polar J&W DB-1701 column (14 % cyanopropylphenyl, 86 % dimethyl polysiloxane) as a primary column, and a non polar J&W DB-5.625 column (95 % dimethyl, 5 % diphenyl polysiloxane) as the confirmatory column. However, as can be seen in Table 5.1, only a few other studies reported the use of these columns, with the J&W DB-1 (100 % dimethyl polysiloxane) and J&W DB-5 (95 % dimethyl, 5 % diphenyl polysiloxane) being more commonly used.

Furthermore, USEPA Method 552.3 (2003) suggested that any other "*fused silica capillary with chemically bonded ("equivalent to" 5% phenylmethylpolysiloxane), or equivalent bonded, fused silica column*" could be used, provided there was "*no inference with any HAAs after running procedure blanks and if equivalent or better sensitivity of HAA peaks is observed.*"

Based on the above information, and what was readily available in the laboratory, a SGE BPX5 (95 % dimethyl and 5 % diphenyl polysilphenylene-siloxane) with dimensions of 30 m × 0.25 mm id × 0.25 µm was used. The SGE BPX5 column was a non polar general purpose column with high temperature range, low column bleed, and was recommended for use in over 80 % of all routine analyses (SGE, 2006).

A derivatised HAA9 standard (100 µg/l each) and a derivatised procedural blank (0 µg/l) were analysed on the GC-µECD using the SGE BPX5 column and the analytical parameters reported in Chapter 3. The resulting chromatograms of the HAA standard showed good peak shapes (*i.e.* narrow and sharp peaks), as shown in Figure 5.1 A below. The procedural blank did not contain any peaks at any of the retention times of the nine HAAs (Figure 5.1 B). Therefore, this column was used for method optimisation and the sample analyses reported in Chapter 6.

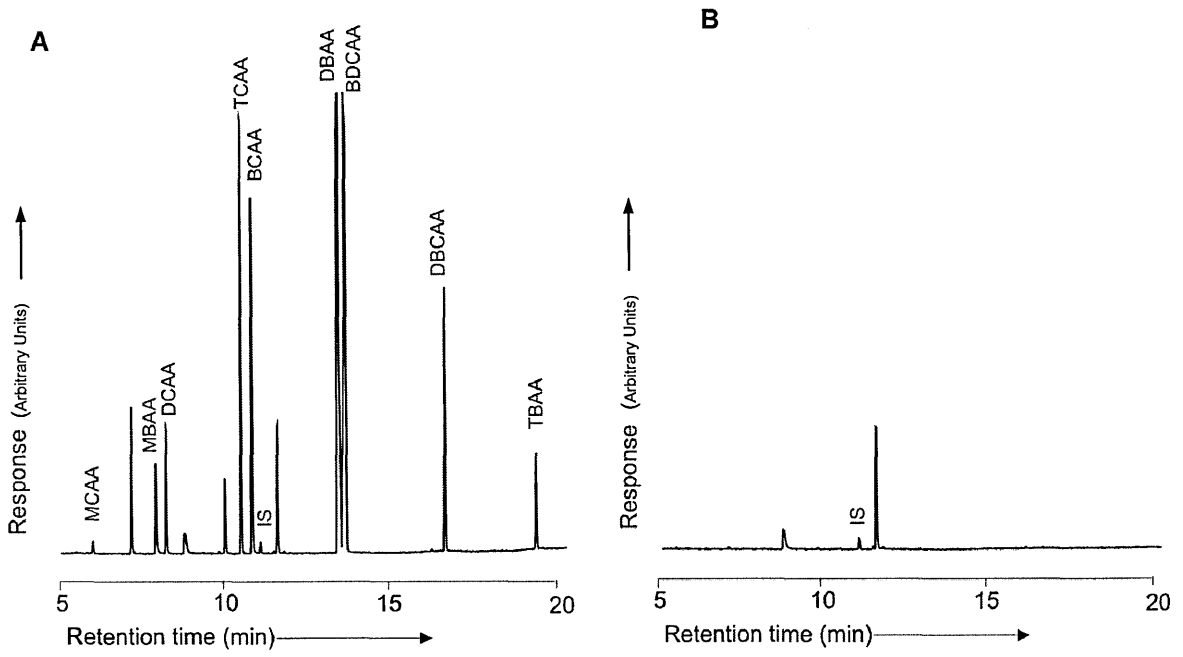


Figure 5.1: Chromatograms, displayed on the same scale, of A) a 100 µg/l derivatised HAA9 standard and a B) derivatised procedural blank (0 µg/l) analysed using the SGE BPX5 column on the GC-µECD.

Issues identified on analysis of treated water samples

Whilst analysing the HAA data obtained from treated water samples, as described in Chapter 6, a significant problem was identified in the use of a SGE BPX5 column with a GC-μECD. On comparing the concentrations measured for DCAA, by GC-μECD and a GC×GC-ToFMS, it became apparent that the GC-μECD was overestimating the DCAA concentrations. It was subsequently established that a compound was co-eluting with DCAA on the SGE BPX5 column. The investigation into the identity of the contaminant peak is discussed in greater detail within Chapter 6.

On further review of the literature it was decided to purchase the confirmation column specified in USEPA Method 552.3, *i.e.* J&W DB-5.625. Whilst of a similar polarity and composition (95 % dimethyl, 5 % diphenyl polysiloxane) as the SGE BPX5, it was shown to separate the DCAA peak from the interfering compound, using the same parameters. This finding illustrates the importance of fully characterising all parameters with the samples of interest and not just standards.

Having been performed prior to the above discovery, the optimisation experiments reported in the Sections 5.3.2.2 and 5.3.2.3, were performed on the original SGE BPX5 column; however, this should not be an issue as the study utilised standards and not treated water samples. However, the determination of the linearity, accuracy, precision and LOD, as reported in Section 5.3.2.4, the optimal J&W DB-5.625 column was used.

5.3.2.2 The optimisation of the oven temperature program on the GC-μECD

As a starting point, the original GC oven temperature settings were taken from USEPA Method 552.3 (2003) and applied to the GC-μECD using a SGE BPX5 column. The initial temperature was held at 40 °C for 10 minutes, raised to 65 °C at 2.5 °C/min, then raised to 85 °C at 10 °C/min, then to 205 °C at 20 °C/min with a post run hold at 210 °C for 7 minutes. The resulting chromatogram obtained from this program showed poor chromatographic resolution, with broad peak shapes, particularly for the early eluting

compounds such as MCAA, DCAA and TCAA, as illustrated by Figure 5.2 A. Broad peaks whose signal to noise ratios were below the minimum reporting levels (MRLs) and had peaks which co-eluted with each other were not acceptable. An optimised linear temperature program was developed using the methodologies reported in the Agilent e-Seminar booklet, 'Method development for capillary GC systems' (Agilent, 2007c). The initial temperature was set at 35 °C and held for 2 minutes after injection, it was ramped up at 5 °C/min to 220 °C.

Visual inspection of the resulting chromatogram showed good peak shapes (*i.e.* narrower and sharper peaks) for the nine HAAs, as shown in Figure 5.2 B, with baseline separation of DBAA and BDCAA. This optimised temperature program also resulted in a shorter GC-run time of 20 minutes, 5 minutes quicker than the earlier program.

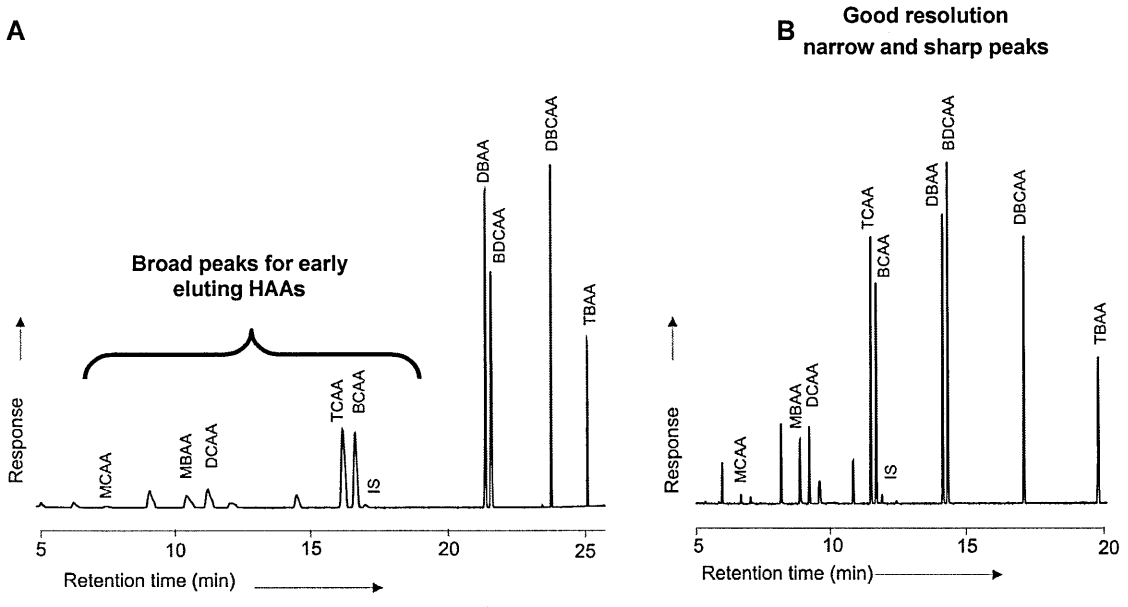


Figure 5.2: Chromatograms, displayed on the same scale, of a derivatised HAA9 standard analysed by GC-μECD using A) the USEPA Method 552.3 oven temperature program and B) optimised linear oven temperature program. Column: SGE BPX5.

As summarised in Table 5.2, the signal to noise ratios of the species of interest showed significantly increased responses for MCAA, MBAA, DCAA, TCAA, BCAA and BDCAA, while the responses of DBAA, DBCAA and TBAA were slightly reduced following optimisation. MCAA showed the greatest increases in response.

Table 5.2: The signal to noise ratios obtained for each species using the original and optimised temperature program.

	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA	IS
Original s/n ratios	25	1052	1205	3405	3557	17009	13254	17885	8712	313
Optimised s/n ratios	135	3455	4166	14990	13066	15058	17457	13574	7540	375
Ratio of optimised / original	5.4	3.3	3.5	4.4	3.7	0.9	1.3	0.8	0.9	1.2

This experiment showed the importance of investigating the temperature programs for the stationary phase and the analytes of interest, as the GC oven temperature influences the chromatographic resolution, peak capacity and the peaks shape of the HAAs. Henceforth, all further HAA experiments were performed using this linear oven temperature program.

5.3.2.3 The optimisation of the GC inlet and detector parameters

The influence of several instrument parameters such as injection type (either splitless or split), injection delay, inlet temperature, make-up gas flow-rate in the detector and detector temperature were investigated on the GC-μECD. Apart from the parameter being investigated, all the other parameters were kept constant.

The influence of injection split-ratios and injection delay was evaluated by observing the relative peak height, signal to noise and peak areas of the target compounds in the resulting chromatograms. However, in the other investigations, a graph of the average peak areas was plotted against each of the HAA species. Peak area was selected because it is directly proportional to the amount of analyte passing through the detector and is more quantitative than the use of peak heights alone.

An initial set of instrument parameters was selected as a baseline for comparison: 150 °C for the inlet temperature, 200 °C for the detector temperature, and a make-up gas flow-rate through the detector of 30 ml/min. A ratio of the peak area for each of the 9 HAAs

relative to the respective peak area from the initial set of parameters was evaluated for each experiment.

Injection type (Split or Splitless)

The influence of splitless, 5:1 and 10:1 split ratios on the relative peak height, signal to noise and peak areas were investigated. Single injections of a derivatised standard (100 µg/l), containing six HAAs, were performed. An Agilent Focus liner with glass wool inserts was used for all three analyses.

The resulting chromatograms can be seen in Figure 5.3. The ratios of the peak heights, peak areas and s/n of the peaks, relative to the splitless injection, are summarised in Table 5.3.

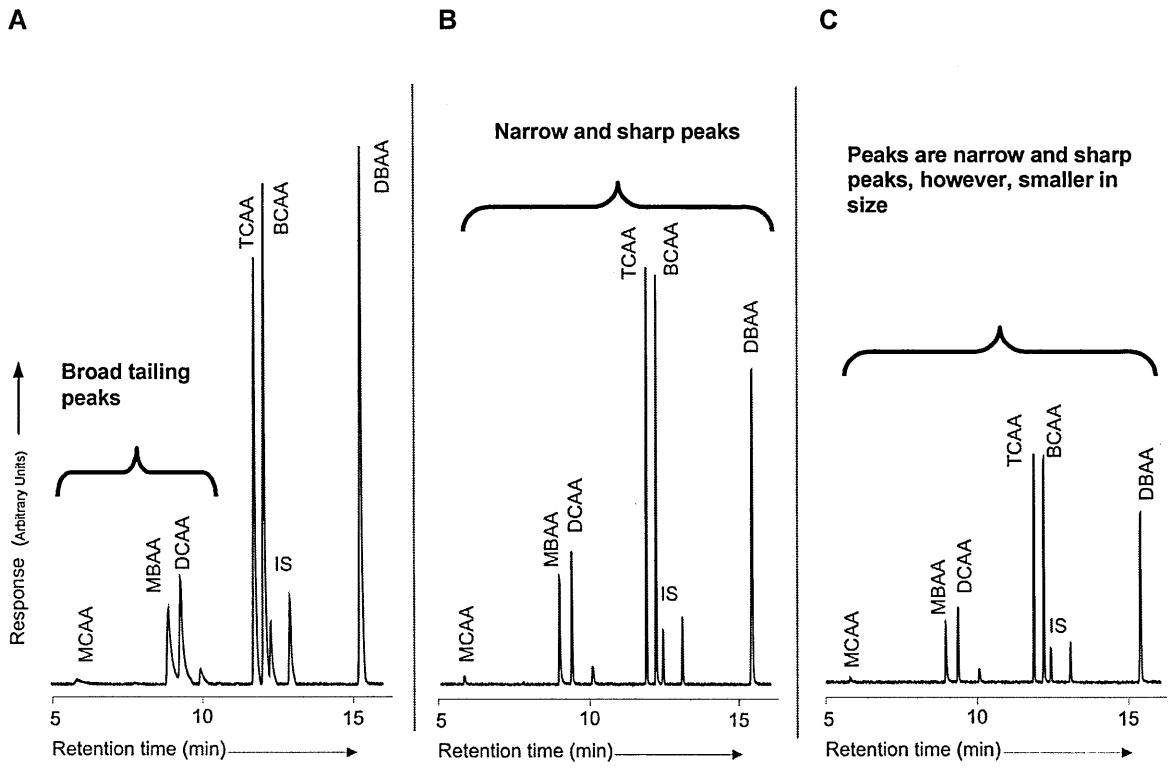


Figure 5.3: Chromatograms displayed on the same scale, of a derivatised HAA6 standard (100 µg/l) and IS (1000 µg/l) run on a GC-µECD in A) splitless injection, B) 5:1 split ratio and C) 10:1 split ratio. Column: SGE BPX5.

The chromatogram resulting from a splitless injection exhibited broad tailing peaks for all 6 HAAs and poor separation of MBAA and DCAA as well as BCAA and the internal standard. The chromatograms from the 5:1 and 10:1 split ratios showed sharp and narrow peaks, with 10:1 split ratio showing lower responses. The splitless injection had the lowest signal to noise ratios particularly for MCAA, MBAA and DCAA.

The peak heights obtained using 5:1 split ratio, when compared to splitless, increased for MCAA, MBAA and DCAA, while the peak height for the IS, BCAA and DBAA reduced. The 10:1 split ratio had a slightly increased peak height response for MCAA (1.09 times), but a reduced response for the other HAAs when compared to the splitless injection.

However, as only a proportion of the HAAs were transferred onto the column using the split injections, the peak areas obtained for the 5:1 split ratio and 10:1 split ratio were smaller then those obtained by splitless injection. The magnitudes of the deviations are summarised in Table 5.3.

Table 5.3: Peak height, peak area and signal to noise ratio of the HAAs obtained using split injection relative to splitless injection.

		MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	IS
Peak Height	*5:1*	1.92	1.42	1.28	0.98	0.82	0.58	0.87
	10:1	1.09	0.76	0.71	0.53	0.44	0.31	0.54
Peak Area	*5:1*	0.35	0.41	0.37	0.42	0.41	0.40	0.37
	10:1	0.22	0.22	0.21	0.23	0.22	0.21	0.23
Peak S/N	*5:1*	1.84	1.47	1.26	0.93	0.88	0.63	0.79
	10:1	1.20	1.19	1.06	0.73	0.70	0.50	0.72

Discussion

The split ratio determines the amount of sample transferred onto the GC capillary column. If the split ratio was low, as in splitless mode, the carrier gas pushes all the volatile sample volume onto the column from the injector. The transfer times from the inlet liner to the column can be significantly long, *i.e.* between 30 - 90 s. This transfer time would result in increased peak broadening and peak tailing. However, if the split ratio was set higher then a smaller proportion of the sample would be transferred onto the column but in a shorter transfer time (< 30 s), and the remainder would be diverted onto the split waste line, resulting in improved peak shape but smaller peak area responses.

Although the peak areas in 5:1 split ratio were considerably lower than splitless, the peak heights were up to twice as large (*e.g.* MCAA). The 5:1 carrier gas split ratio was therefore selected for this study because it provided the best overall package of good peak shapes and peak heights, compared to the poorer peak shapes and resolution in the splitless mode and the lower sensitivity with the 10:1 split ratio.

Injection delay

The influence of a pre- and post-injection delay, *i.e.* the time that the syringe needle remains in the hot GC-injection port before and after injection, were investigated. A 3 second pre- and post-injection delay was compared with a fast injection which had no injection delay.

The resulting chromatograms, relative peak area, peak height and signal to noise ratios, for the chromatograms are shown in Figure 5.4 and Table 5.4.

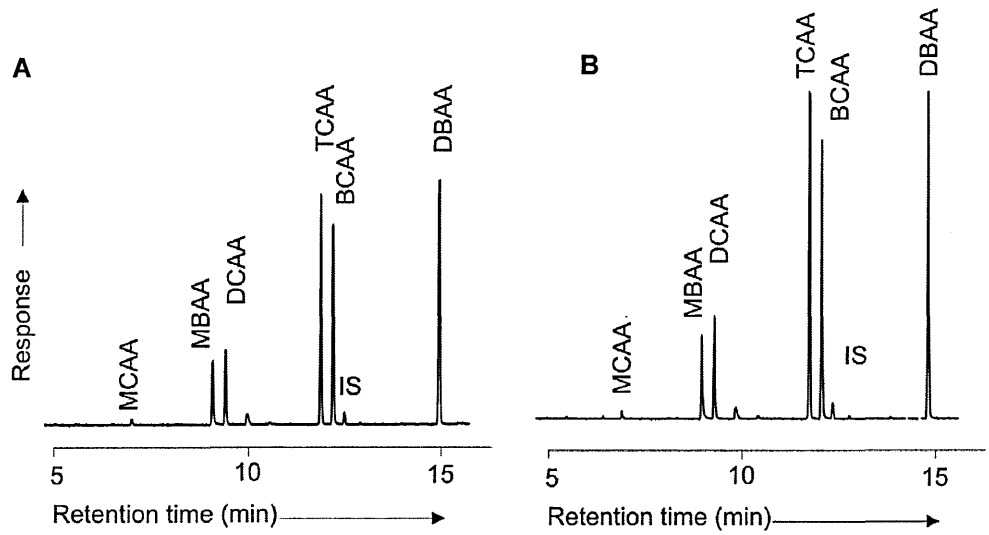


Figure 5.4: Chromatograms of a HAA6 derivatised standard (100 µg/l) run on A) without an injection delay and B) with a pre- and post-injection delay of 3 seconds. Column: SGE BPX5. Both chromatograms have the same response scale.

Both Figure 5.4 and Table 5.4, show that the pre- and post-injection delay resulted in an improved response (as measured by the peak height) of 1.42, 1.41 and 1.48 times for the later eluting TCAA, BCAA and DBAA, respectively. The peak heights of the more volatile MCAA, MBAA and DCAA also increased. Furthermore, an injection delay resulted in an increase in peak areas between 1.26 - 1.31 times for these species. The signal to noise ratio of each of these HAAs increased by 1.04 - 1.32 times, with TCAA, BCAA and DBAA showing the greatest increase.

Table 5.4: Peak height, peak area and signal to noise ratio relative to 'no injection' delay.

	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	IS
Peak height	1.26	1.31	1.38	1.42	1.41	1.48	1.31
Peak area	1.29	1.28	1.26	1.31	1.28	1.29	1.25
s/n ratio	1.04	1.08	1.13	1.24	1.32	1.25	1.26

Discussion

The derivatised HAA standards, introduced in the liquid state, were vaporised on the injector liner and subsequently instantly transferred on to the column. This evaporation process can lead to a mass discrimination of the high molecular weight HAAs either inside the needle or on the needle tip (Agilent, 2005). It is hypothesised that the extra dwell time of the syringe needle in the injector inlet, provides sufficient time for the high molecular-weight HAAs to vaporise, thus increasing their transfer efficiency and subsequent overall response (Agilent, 2005). A 3 sec pre- and post-injection delay was, therefore, used in all further analyses.

Inlet Temperature

Four inlet temperatures (150, 200, 250 and 300 °C) were investigated by performing duplicate injections of a HAA9 derivatised standard (100 µg/l) at each temperature.

The results, summarised in Figure 5.5, showed that the average peak areas of six of the HAAs, *i.e.* MCAA, MBAA, DCAA, TCAA, BCAA and DBAA, gradually increased with an increase in inlet temperature from 150 °C to 300 °C. The response for BDCAA shows a gradual increase up to 250 °C. Any further increase in inlet temperature did not increase the peak area. The area for DBCAA increases at 200 °C, however by 300 °C, it is 0.81 times smaller than at 150 °C. The area of TBAA increases at 200 °C and at 250 °C, but has significantly reduced at 300 °C. The relative magnitude of the peak areas are summarised in Table 5.5.

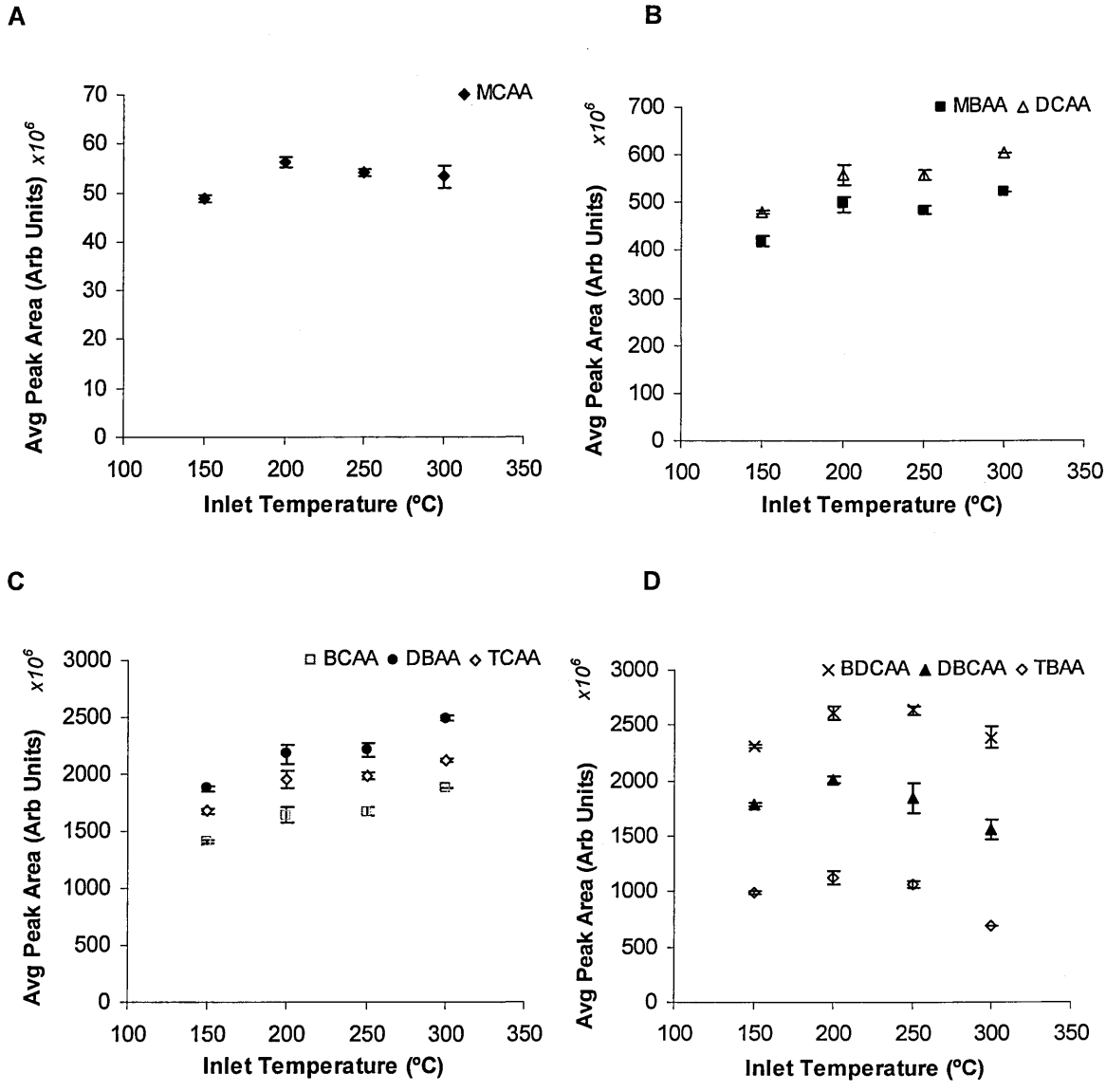


Figure 5.5: The response of HAAs to the changes in inlet temperature A) MCAA B) MBAA and DCAA C) TCAA, BCAA, DBAA and D) BDCAA, DBCAA and TBAA. Error bars are the spread of the two data points, n=2.

Table 5.5: Relative peak areas for each HAA at various inlet temperatures relative to the peak areas measured at 150 °C.

	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
200 °C	1.15 ± 0.02	1.18 ± 0.04	1.17 ± 0.04	1.17 ± 0.04	1.16 ± 0.04	1.16 ± 0.04	1.13 ± 0.02	1.13 ± 0.01	1.14 ± 0.03
250 °C	1.11 ± 0.02	1.16 ± 0.04	1.17 ± 0.04	1.18 ± 0.04	1.18 ± 0.05	1.18 ± 0.05	1.14 ± 0.03	1.03 ± 0.08	1.08 ± 0.02
300 °C	1.14 ± 0.04	1.24 ± 0.02	1.26 ± 0.02	1.26 ± 0.02	1.33 ± 0.02	1.32 ± 0.03	0.99 ± 0.04	0.81 ± 0.10	0.62 ± 0.09

Discussion

The general trend showed that at the highest inlet temperatures, the higher molecular weight HAAs such as TBAA have reduced responses. This could be because of an increase in thermal degradation, decomposition and hydrolysis during the vaporisation of the HAA standards in the hot GC-inlet (Ma *et al.*, 2005; Wu *et al.*, 2001). However, as future studies intended to measure HAA9 and not just HAA6, the only two viable temperatures were 200 °C and 250 °C. Furthermore, a brief survey of literature inlet temperature for the analysis of HAAs revealed that inlet temperatures of 200 - 210 °C were commonly used (USEPA, 2003a; Yang *et al.*, 2005). Therefore, 200 °C was utilised as the inlet temperature for the analysis of HAAs in all further experiments.

Detector make-up gas flow-rate

Six make-up gas flow-rates of 10, 15, 30, 45, 60 and 75 ml/min were examined. Duplicate injections of a HAA9 derivatised standard (100 µg/l) were performed at each flow-rate.

The resulting chromatograms for each flow-rate all showed good peak shapes. The baseline signals for the chromatograms for the lower make-up flow-rates were higher than those obtained at the higher flow-rates. The areas obtained for each species, at each flow-rate, are shown in Figure 5.6 and the relative peak area for the chromatograms have been summarised in Table 5.6.

It can be seen that below 30 ml/min there was a significant increase in the peak areas of all the species, particularly MCAA. Above 30 ml/min, all HAAs had a much lower response. An examination of the chromatograms for the 10 ml and 15 ml flow-rates showed elevated levels of baseline noise and peak tailing.

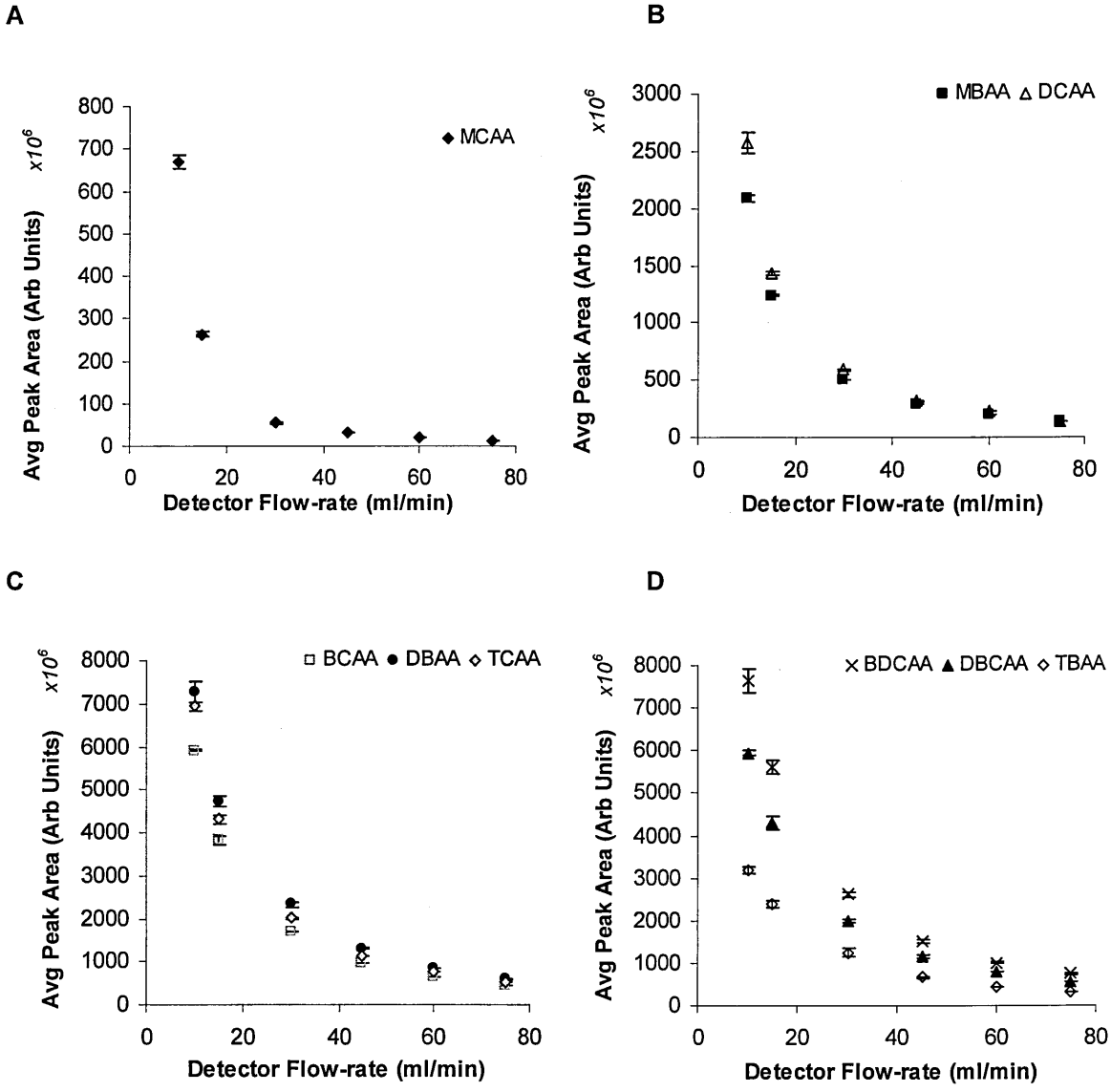


Figure 5.6: The response of the HAAs to the changes in detector make-up flow-rates for A) MCAA B) MBAA and DCAA C) TCAA, BCAA, DBAA and D) BDCAA, DBCAA and TBAA. Error bars are the spread of the two data points.

Table 5.6: The ratio of the peak areas of the HAA responses, relative to 30 ml/min, observed for make-up gas flow-rates of 10, 15, 45, 60 and 75 ml/min.

	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
10 ml/min	12.20	4.12	4.38	3.44	3.48	3.11	2.92	2.99	2.55
	± 0.05	± 0.04	± 0.02	± 0.01	± 0.01	± 0.05	± 0.04	± 0.02	± 0.09
15 ml/min	4.79	2.44	2.44	2.14	2.25	2.03	2.15	2.17	1.92
	± 0.05	± 0.02	± 0.01	± 0.02	± 0.02	± 0.04	± 0.03	± 0.04	± 0.09
45 ml/min	0.57	0.58	0.53	0.56	0.57	0.56	0.57	0.57	0.53
	± 0.05	± 0.02	± 0.05	± 0.01	± 0.01	± 0.03	± 0.03	± 0.05	± 0.09
60 ml/min	0.33	0.39	0.39	0.38	0.38	0.37	0.39	0.40	0.36
	± 0.04	± 0.02	± 0.04	± 0.01	± 0.01	0.03	± 0.02	± 0.03	± 0.09
75 ml/min	0.19	0.26	0.24	0.26	0.26	0.25	0.28	0.28	0.26
	± 0.06	± 0.02	± 0.05	± 0.01	± 0.01	± 0.03	± 0.02	± 0.03	± 0.09

Discussion

The overall trend was that for all species, the lower the make-up gas flow-rate, the greater the signal response. It is known that the make-up gas has a substantial effect on the quantity of electrons detected (Jiří, 1976). The make-up gas would be ionised by the radioactive ^{63}Ni to form free electrons which provide a background current for the detector. These electrons would be captured by the electronegative compounds from the column eluents resulting in a decrease in the background current, hence providing a response. As the gas flow-rate is reduced, the residence time of the electronegative compounds within the detector would increase resulting in larger signals. However, at lower flow-rates, other complex secondary reaction can occur within the detector and deposition of the molecules could contaminate the detector. Contaminated ECDs can lead to loss of sensitivity, trailing peaks, and erratic baselines (Loconto, 2006; McNair *et al.*, 2009). The manufacturers have recommended a make-up gas flow-rate of 30 - 60 ml/min through the detector (Agilent, 2003). Other studies on GC-μECD have also reported higher nitrogen flow-rates of 46 ml/min by Nikolaou *et al.,* (2002 a) and 56 ml/min by Malliarou *et al.* (2005). The

USEPA Method 552.3 (2003) used a lower flow-rate at 20 ml/min; however, a different make-up gas was used (95 % Argon / 5 % methane).

Taking all the factors into account, a 30 ml/min make-up flow-rate was deemed most appropriate to ensure suitable responses of the HAAs without contaminating the source.

Detector Temperature

Four detector temperatures (150, 170, 200 and 230 °C) were investigated. Duplicate injections were performed at each temperature. The mean peak areas obtained for each species, at each detector temperature, are presented in Figure 5.7. These average areas were then referenced to the average areas obtained at the lowest temperature of 150 °C. The normalised values obtained are presented in Table 5.7.

Table 5.7: Ratios of the peak areas of the HAAs, relative to 150 °C, observed for the detector temperatures of 170, 200 and 230 °C.

	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
170 °C	1.71 ± 0.01	1.07 ± 0.004	1.16 ± 0.01	1.07 ± 0.01	1.06 ± 0.03	1.04 ± 0.01	1.03 ± 0.01	1.04 ± 0.02	1.06 ± 0.02
200 °C	1.58 ± 0.02	1.05 ± 0.03	1.23 ± 0.01	1.06 ± 0.01	1.02 ± 0.01	0.98 ± 0.01	0.92 ± 0.01	0.89 ± 0.02	0.89 ± 0.02
230 °C	1.96 ± 0.01	1.13 ± 0.02	1.38 ± 0.02	1.06 ± 0.04	1.04 ± 0.03	1.01 ± 0.01	0.84 ± 0.03	0.71 ± 0.12	0.63 ± 0.09

MCAA, followed by DCAA, showed the greatest increase in response following an increase in temperature from 150 to 230 °C. The peak areas of TCAA, BCAA and DBAA did not alter significantly on any change in detector temperature. However, peak areas of BDCAA, DBCAA and TBAA were strongly influenced by the change in the detector temperature. Increasing the temperature from 150 to 170 °C had a small increase in response; however on increasing to 200 °C, the peak areas decreased for BDCAA, DBCAA and TBAA, respectively. A further increase, to 230 °C, resulted in a further decrease in the response for BDCAA, DBCAA and TBAA, respectively.

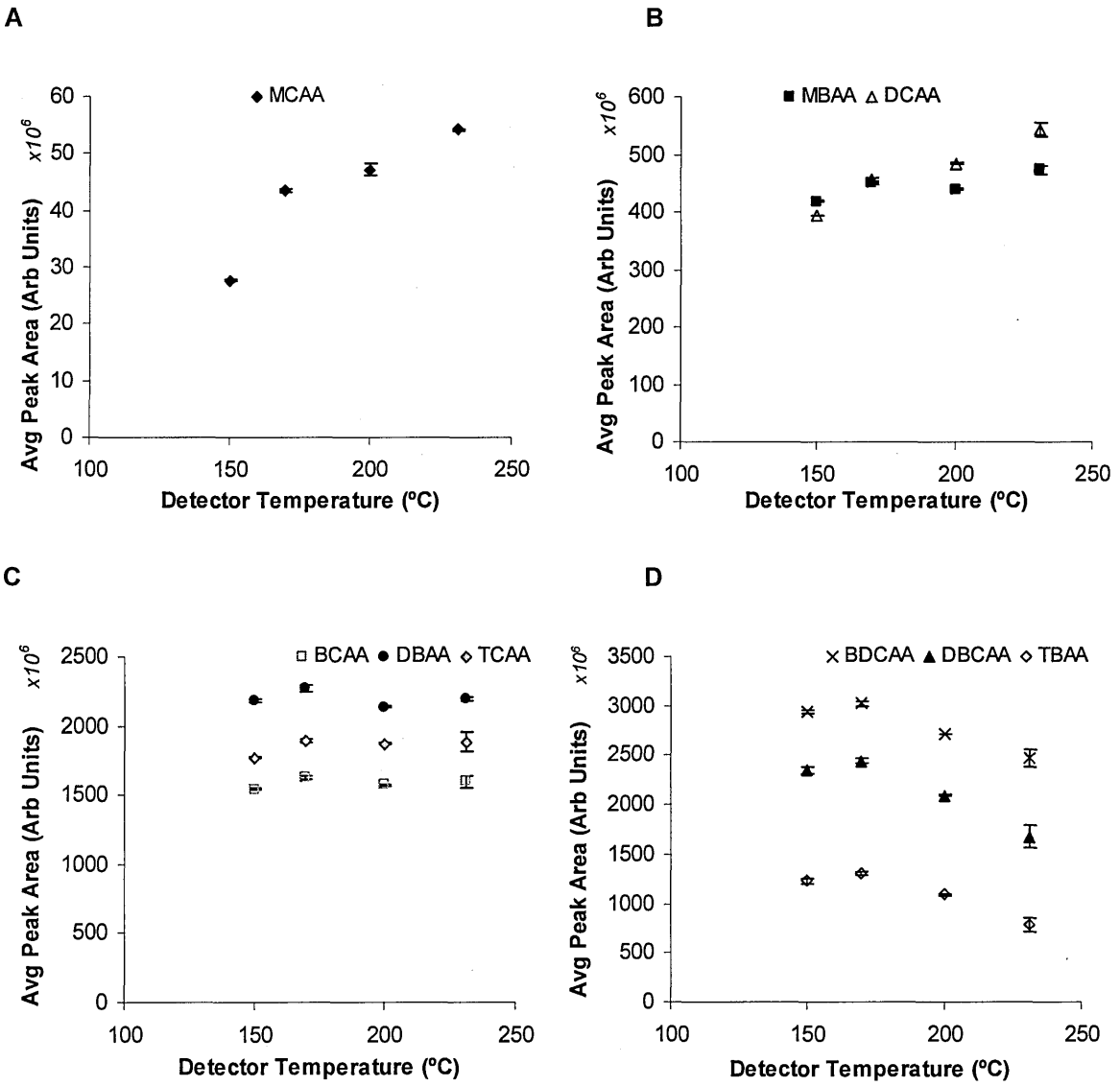


Figure 5.7: The response of HAAs to the changes in detector temperature for A) MCAA B) MBAA and DCAA C) TCAA, BCAA, DBAA and D) BDCAA, DBCAA and TBAA. Error bars are the spread of the two data points, n=2.

Discussion

The detector temperature influences each of the HAAs differently. The area response increased for lower mass HAAs and decreased for the higher mass HAAs. It has been reported that the detector temperature influences the energy of the electrons from the ^{63}Ni radioactive source and electron capture mechanism of the detector (Jiří, 1976). The overall structure of the compounds could determine the influence of the detector temperature and the effects of the increased electron energy (Zlatkis *et al.*, 1981). At higher temperatures thermally labile HAAs, such as TBAA, BDCAA and DBCAA, could decompose at the higher electron energies resulting in a loss of response.

A quick review of literature on the HAAs analytical methods showed that a detector temperature of 290 °C - 300 °C was commonly used (Nikolaou *et al.*, 2002a; USEPA, 2003a). However, based on the results of this study, the most appropriate detector temperature was selected as 230 °C as it resulted in the highest overall HAA responses.

Summary

In summary, the results showed that the detector sensitivity was most significantly affected by the make-up gas flow-rate to the detector. The injector temperature, injection delay, split ratios and detector temperature had a smaller influence on the response. As reported earlier, the experiments in the Sections 5.3.1.2 and 5.3.1.3, were performed using a SGE BPX5 column; however, the findings were then applied to the J&W DB-5.625 column for the determination of the linearity, accuracy, precision and LOD (Section 5.4.1.3).

5.3.2.4 Determining the linear range, precision, accuracy and limit of detection of the GC-μECD for individual HAAs.

Linearity

The linearity of the GC-μECD was evaluated from a 6-point calibration curve, produced from a series of derivatised calibrations standards analysed in duplicate. The calibration curves were generated by plotting the areas ratios (Area of the HAA/Areas of the IS) against the concentrations of the calibration standards within the range of 0 - 100 μg/l for each HAA.

As illustrated in Figure 5.8, good linearity was obtained for each species, with correlation coefficients $R^2 > 0.9890$, as reported in Table 5.8. The regression lines were forced through the origin.

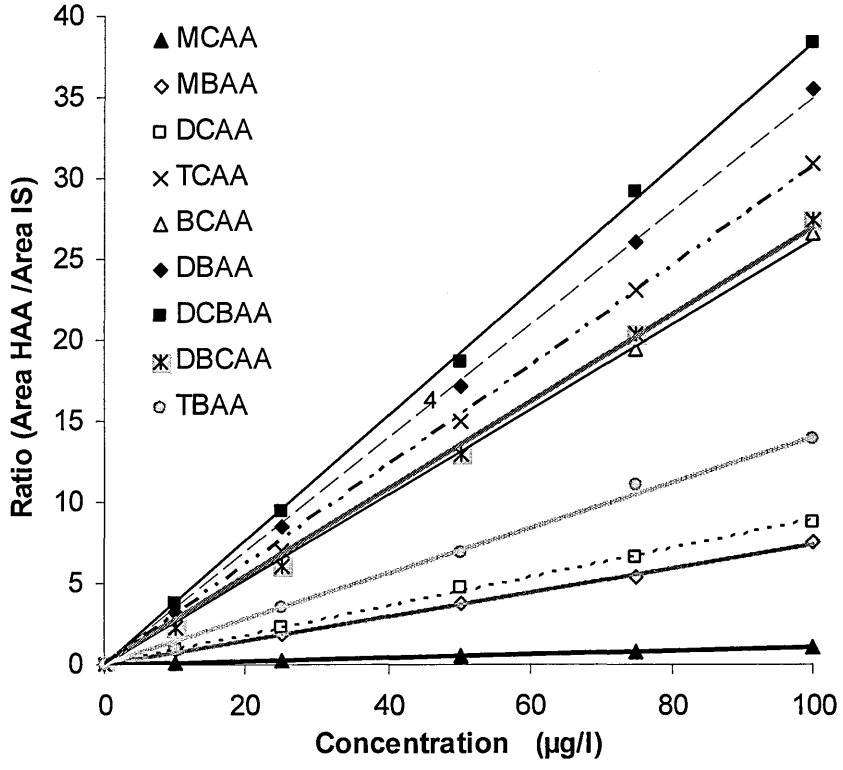


Figure 5.8: The linear calibration plots for the nine HAAs obtained by GC-μECD (DB 5.625 column).

Precision

As discussed in Section 4.3.2.7, the precision of the analytical procedure is measured by the RSD, which may be considered at three levels: repeatability (intra-day precision), intermediate precision (inter-day precision) and reproducibility (inter-laboratory precision in a collaborative study).

In this study, the repeatability of the instrument, *i.e.* variation in measurements by the instrument on the same day, was evaluated as follows: A single HAA9 derivatised standard (~ 4 ml) at a concentration of 100 µg/l per HAA was aliquoted equally into ten 200 µl amber glass vials, using an automatic pipette. 1 µl aliquots from each of ten replicate vials were then analysed on the GC-µECD on the same day. The standard deviation (σ_{n-1}) of the peak areas was calculated for all the 9 HAAs from the ten replicates. The precision of a 50 µg/l standard (n=5) and a 1 µg/l (from the LOD experiments below, n=7) were also determined in a similar manner. The results have been reported in Table 5.8.

The precision of the GC-µECD for the HAAs was found to be between 1.7 - 4.6 % at 100 µg/l, 1.3 - 4.2 % at 50 µg/l and 1.1 - 4.3 % at 1 µg/l, respectively. These results were well within the acceptable precision of ± 20 % for analytical experiments for HAA analyses (USEPA 552.3, 2003). For comparison the USEPA Method 552.3 reported a similar precision (RSD) of 0.52 - 4.7 % for a 10 µg/l derivatised standard and 0.36 - 4.1 % for a 1 µg/l standard.

Accuracy

The accuracy of the method, which is the degree of closeness of a measured concentration to an equivalent point on the calibration curve, was also investigated. A single HAA9 derivatised standard (~ 4 ml) at a concentration of 100 µg/l was separated into 10 equal portions (~ 0.4 ml) and transferred into 200 µl amber glass vials using an automatic pipette. These 10 replicate vials were then analysed on the GC-µECD, on the

same day, using the parameters described in Chapter 3. The concentrations of each species in each standard were evaluated against a 7-point calibration curve. The accuracy at 50 µg/l was also evaluated except only 5 vials were analysed. The results of the LOD experiments were used to determine the accuracy at 1 µg/l (n=7). The results have been summarised in Table 5.8.

The accuracy on the GC-µECD for the HAAs was found to be between 93.2 - 106.3 % at 100 µg/l, 89.3 - 109.3 % at 50 µg/l and 75.7 - 129.5 % at 1 µg/l, respectively. In USEPA Method 552.3 (2003) the accuracy was described in terms of 'analyte recovery', where the mean recovery with the standard deviation constitutes a measure of accuracy. These results obtained here were within the acceptable analyte recoveries of ± 20 % at the mid-range standard of the calibration curve (USEPA 552.3, 2003). The range of values obtained for 1 µg/l was relatively higher, compared to the other two concentrations (50 and 100 µg/l). The USEPA Method 552.3 reported an accuracy of 98.2 - 111 % for a 10 µg/l derivatised HAA9 standard and an accuracy of 92.2 - 128 % for the 1 µg/l standard. Any method with recoveries above ± 30 % would not be acceptable (USEPA 552.3, 2003).

Limits of Detection

The LOD of each species was determined experimentally using seven replicates on each of two derivatised HAA standards (0.1 and 1 µg/l) that were extracted and analysed over a period of three days. The concentration of each species in each standard was calculated using the 6-point calibration curve for each HAA. A mean concentration for each HAA was calculated. The standard deviations of each species from the mean values was then determined. The LOD was then calculated using the equation from USEPA Method 552.3 (2003), as illustrated by the Equation 5.1.

$$LOD = \sigma_{n-1} \times 3.143 \qquad \text{Equation 5.1}$$

σ_{n-1} is the standard deviation

3.143 is a Students t value for 99 % confidence level for 7 replicates

As reported in Table 5.8, and as anticipated, MCAA has the highest detection limit of 0.28 µg/l while the other HAAs have LODs between 0.09 - 0.24 µg/l. The USEPA Method 552.3 also reported MCAA with the highest detection limits of 0.17 µg/l, while the remaining HAAs were found with detection limits of 0.01 - 0.11 µg/l. The total LOD for the nine HAAs was 1.30 µg/l. For comparison, the LOD standards were also analysed at Cranfield University and found to be 1.44 µg/l for the nine HAAs (Bougeard, 2009).

Method Reporting Levels (MRL)

The MRL of each species was also determined using the USEPA Method 552.3, which recommends it is calculated as at least 3 times the LOD value. The MRL is the "*threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample".* The results showed that MRLs in this study were between 0.15 - 0.83 µg/l. This was higher than the USEPA Method 552.3 (0.03 - 0.51 µg/l), but lower than that recommended by USEPA DBP/ICR Analytical Method, *i.e.* between 1 - 4 µg/l of the HAAs (USEPA, 1996a).

Retention Time Precision

The retention time precision was also evaluated by calculating the relative standard deviation of the each of the HAA peaks, as recommended by USEPA Method 552.3 (2003). As reported in Table 5.8, the RSD ranged from 0.004 - 0.050 % which were comparable to the USEPA Method 552.3 findings of 0.000 - 0.040 %.

Summary

These experiments have indicated that the analysis of HAA9 standards, using a DB.5.625 column prior to an Agilent GC-µECD, performs at a level that approximates those reported for USEPA Method 552.3. The linearity for each HAA had a correlation coefficient R^2 > 0.9890; precision for the HAAs between 1.7 - 4.6 % at 100 µg/l, 1.3 - 4.2 % at 50 µg/l and 1.1 - 4.3 % at 1 µg/l; accuracy of between 93.2 - 106.3 % at 100 µg/l, 89.3 - 109.3 % at

50 µg/l and 75.7 - 129.5 % at 1 µg/l; the total LOD for the nine HAAs was 1.30 µg/l; the MRL of between 0.15 – 0.83 µg/l and retention time RSD of from 0.004 - 0.050 %.

Table 5.8 The mean column retention times, linearity correlation coefficient, accuracy, repeatability, LODs and MRLs and of nine HAAs obtained using the GC-μECD.

Compound	Mean retention time (min)	Retention time RSD [1] (%)	Correlation coefficient [2] (R^2)	Accuracy [3] (%)			Repeatability RSD [4] (%)			LOD [5] (μg/l)	MRL[6] (μg/l)
				1 μg/l *n=7*	50 μg/l *n=5*	100 μg/l *n=10*	1 μg/l *n=7*	50 μg/l *n=5*	100 μg/l *n=10*	*n=7*	*n=7*
MCAA	6.31	0.050	0.9988	125.6	109.3	93.2	3.75	3.21	2.01	0.277 (1.0)	0.83
MBAA	8.21	0.022	0.9968	102.6	108.5	95.6	1.08	2.97	3.02	0.187 (1.0)	0.56
DCAA	8.56	0.022	0.9981	108.1	107.4	99.1	2.89	3.77	2.32	0.087 (0.1)	0.26
TCAA	10.93	0.010	0.9957	120.6	97.6	102.3	1.14	3.05	1.66	0.159 (1.0)	0.48
BCAA	11.12	0.008	0.9989	129.5	104.3	99.4	2.76	4.16	3.75	0.069 (0.1)	0.21
DBAA	13.67	0.005	0.9988	89.9	105.5	100.2	1.91	2.63	2.87	0.157 (1.0)	0.47
BDCAA	13.86	0.006	0.9912	102.6	101.0	103.3	1.56	3.31	4.29	0.078 (0.1)	0.23
DBCAA	16.77	0.004	0.9890	75.7	89.3	104.8	1.60	2.78	4.59	0.049 (0.1)	0.15
TBAA	19.61	0.009	0.9948	77.8	92.6	106.3	4.30	1.27	3.54	0.236 (1.0)	0.71
IS	11.34	0.015	-	-	-	-	-	-	-	-	-

[1] The % RSD of the retention times of 1 μg/l (n=7) derivatised HAA9 standard,

[2] The linear range for 1 - 100 μg/l of derivatised HAA9 standards,

[3] The accuracy of 1 μg/l (n=7), 50 μg/l (n=5) and 100 μg/l (n=10) derivatised HAA9 standard,

[4] The precision of 1 μg/l (n=7), 50 μg/l ((n=5) and 100 μg/l (n=10) derivatised HAA9 standard,

[5] The LOD derived from a 1 μg/l and/or 0.1 μg/l derivatised HAA9 standard (n =7); the brackets indicate the concentration of the standard used,

[6] The MRL corresponds to the minimum reporting level, a threshold for quantification in a sample recommended by USEPA Method 552.3 to be 3 times LOD.

5.3.3 The analysis of HAAs with a GC-MS in electron impact ionisation mode

Having established a baseline performance for HAAs using a GC-μECD system the potential of mass spectrometry for HAA analyses was explored. GC-MS has been a 'gold standard' instrument commonly used in many analytical laboratories. The analysis of HAAs by GC-MS, in standard electron impact ionisation (EI) mode, utilises specific fragment ions for quantitation. The chromatograms of these ions provide better specificity, selectivity and identification of the HAAs than the total ion chromatogram. In the literature, the quantitation ion *m/z* 59 $[COOCH_3]^+$ is used for all nine HAAs and *m/z* 75 is used for the internal standard (IS), 1,2,3 trichloropropane (Xie, 2003).

A series of six derivatised HAA calibration standards (0, 10, 25, 50, 75, 100 μg/l) and procedural blanks were analysed in duplicate on an Agilent 6890-5973 N GC-MS. One injection was performed in full-scan mode (*m/z* 33 - 330) for the identification of the HAAs whilst the other was performed in selected ion monitoring (SIM) mode using the ions *m/z* 59 and *m/z* 75 $[C_3H_4Cl]^+$ for the quantitation of the HAAs and IS. The SIM mode was utilised as it is generally known to provide up to a ten fold increase in sensitivity and therefore results in superior detection limits primarily through a reduction in noise (Feigel *et al.*, 1999). The remaining instrument parameters used in this study have been reported in Section 3.2.4.

Results obtained in the full scan mode (m/z 33-330)

Typical total ion chromatograms (TIC) for a derivatised HAA6 standard (100 μg/l) and a procedural blank (0 μg/l) obtained in full-scan mode are shown in Figure 5.9. Visual inspection of both chromatograms showed hundreds of large peaks present in both the standard and blanks. Hence, HAA peaks could not be identified or resolved in the TIC.

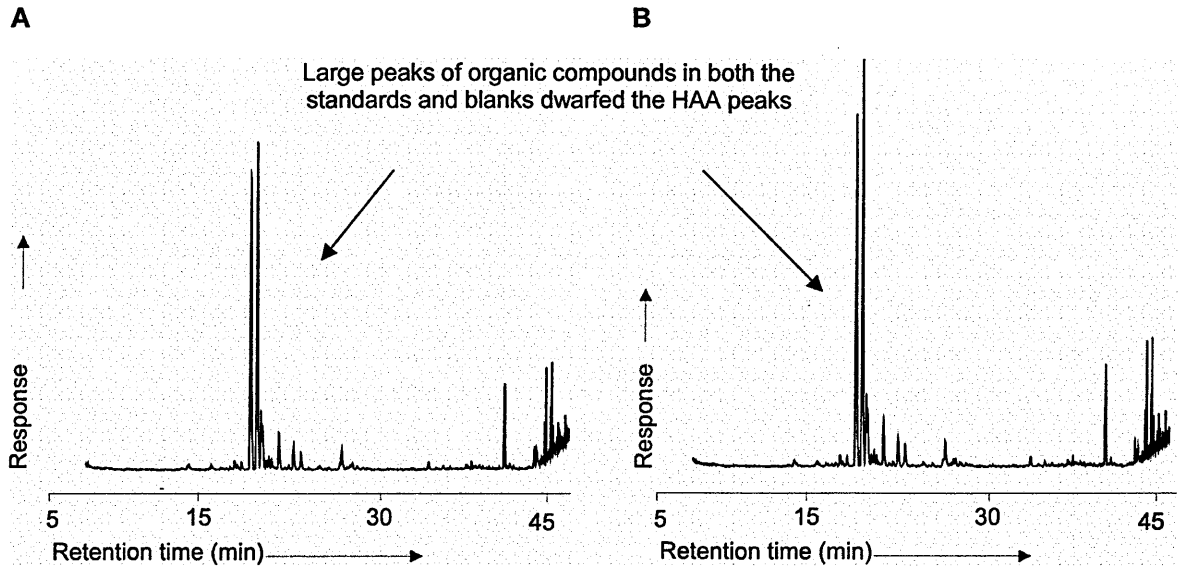


Figure 5.9: Total ion chromatograms, displayed on the same scale, obtained on an Agilent 6890-5973 N GC-MS (EI) in full scan mode (m/z 33 - 330) of A) a derivatised procedural blank (0 µg/l) and B) a derivatised HAA6 standard at a concentration of 100 µg/l.

The HAA quantitation ion (*m/z* 59) and the IS quantitation ion (*m/z* 75) were extracted from the TIC. The resulting partially reconstructed ion chromatograms (RIC) for the derivatised HAA standards and procedural blank are shown in Figure 5.10.

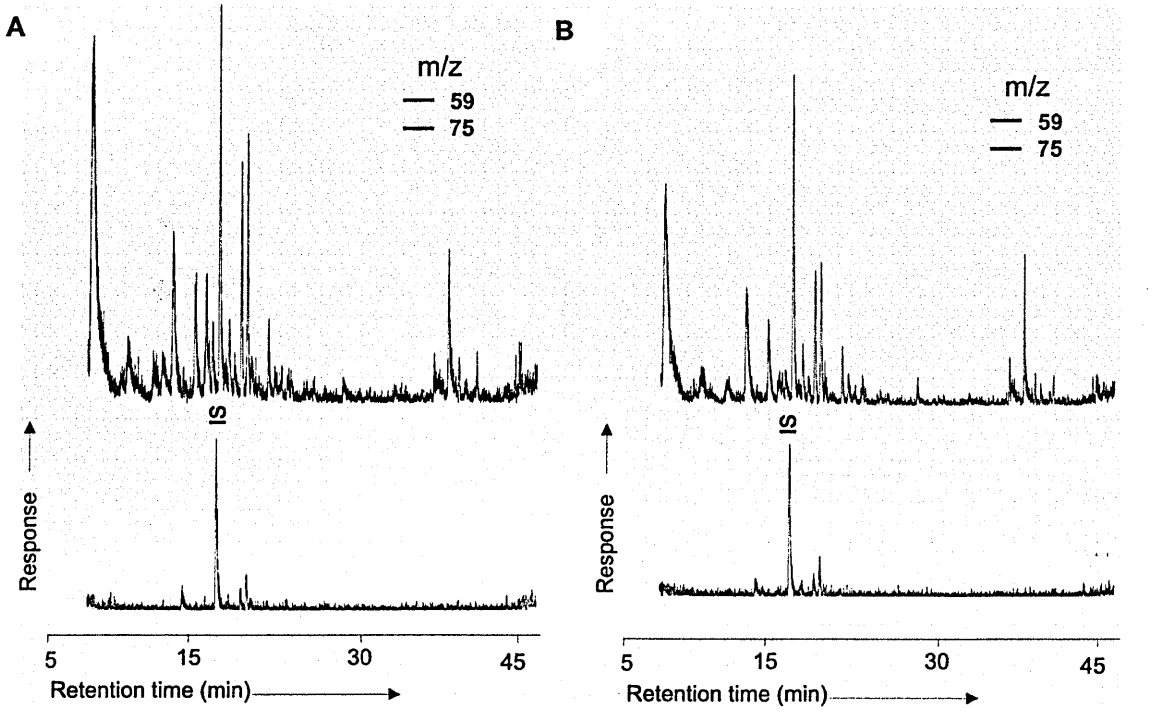


Figure 5.10: Partially reconstructed ion chromatograms, displayed on the same scale, obtained by Agilent 6890-5973 N GC-MS (EI) in full scan mode (m/z 33-330) of A) a derivatised HAA6 standard at a concentration of 100 µg/l and B) a derivatised procedural blank (0 µg/l).

Examination of the extracted chromatograms for *m/z* 75 shows that the internal standard is well separated and easily identifiable in both the HAA6 standard sample and procedural blank. However, the extracted chromatograms for *m/z* 59 show the presence of large contaminant peaks, in nearly equivalent abundance for both the derivatised HAA standard and procedural blank. These contaminant peaks prevent the identification and quantitation of the six HAA compounds of interest. Ideally, the chromatogram of the procedural blanks should not contain any major contaminant peaks, as it should not contain any compounds, except the internal standard. Their presence in both the standard sample and procedural blank would indicate that the derivatisation process is most likely introducing the contamination. The *m/z* 59 ion, is generic for the $[COOCH_3]^+$ fragment, which would suggest that either prior or during derivatisation a number of carboxylic acid or ester containing species were present. The use of the fragment ion (*m/z* 59) did not, in this case, further improve the selectivity of HAAs over the TIC.

Results obtained in SIM mode (m/z 59)

Typical chromatograms (*m/z* 59), collected in selected ion monitoring mode, of a derivatised HAA6 calibration standard (100 µg/l) and a derivatised procedural blank (0 µg/l) are shown in Figure 5.11. The resulting chromatograms showed many large peaks with abundant *m/z* 59 ions, similar to the RICs shown earlier in Figure 5.10. As in the TIC chromatograms, these peaks prevented the quantitation of HAAs, as resolution of the HAAs from the interfering peaks was not possible.

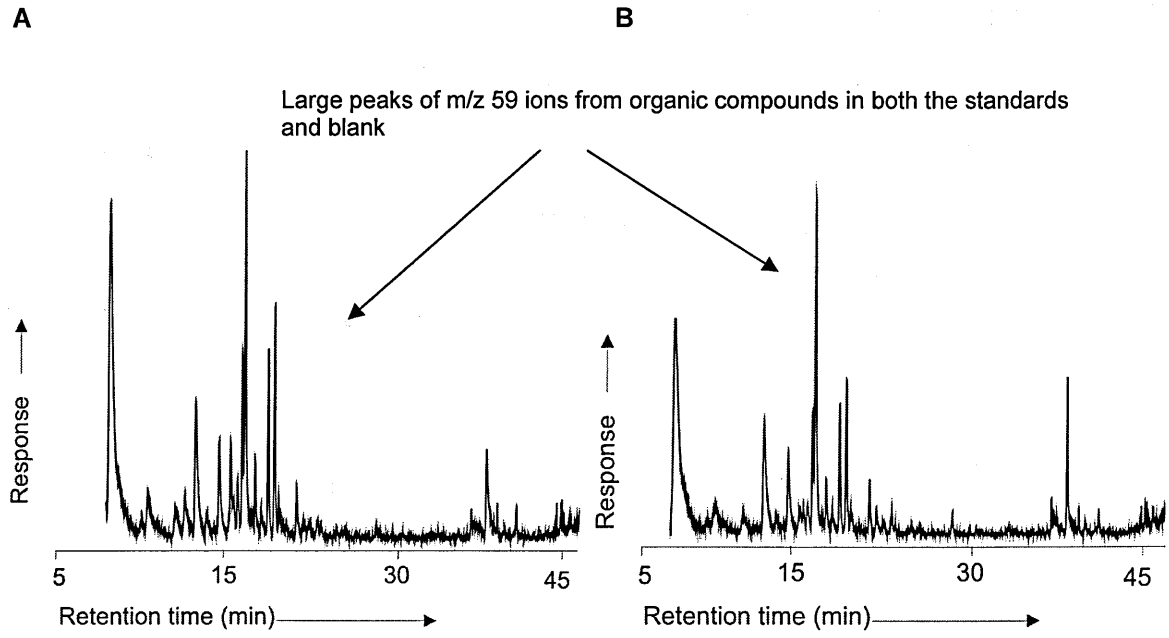


Figure 5.11: Chromatograms collected in SIM mode (m/z 59), displayed on the same scale, of A) a derivatised HAA9 standard at 100 µg/l and B) a derivatised procedural blank (0 µg/l).

In order to confirm the findings, these samples were also run at Cranfield University on another GC-MS system, a Perkin Elmer Turbomass MS operated in EI mode. The results were found to be comparable, indicating that the issue was with the sample preparation procedure and not the instrumentation parameters.

Summary

Based on the results obtained at both institutions on the same samples, and in contrast to the results previously reported by Xie (2001), HAAs could not be accurately identified nor quantified by GC-MS (EI). No further HAA analyses were performed by GC-MS (EI). Further work would be required to identify the disparity between Xie and this study in order to remove the source of the contaminant peaks introduced during the 6-hour sample preparation and derivatisation process. As there are a number of individual steps in the process where the contamination can be introduced, it needs to be established if it is occurring in either the analysis, derivatisation or extraction phases. Further work would focus on analysing HAA methyl-ester standards, which can be purchased from Sigma Aldridge, on the GC-MS (EI) to isolate the analysis phase for evaluation. Direct derivatisation and analysis of HAA standards would eliminate the extraction phase from

the process enabling an evaluation of the derivatisation phase. Once the phase which introduces the contamination has been identified, a methodically elimination of all the possible sources of contamination processes, such as the cleaning of the glassware, the purity of the solvents and so on, need to be performed.

5.3.4 The analysis of HAAs using GC×GC-ToFMS

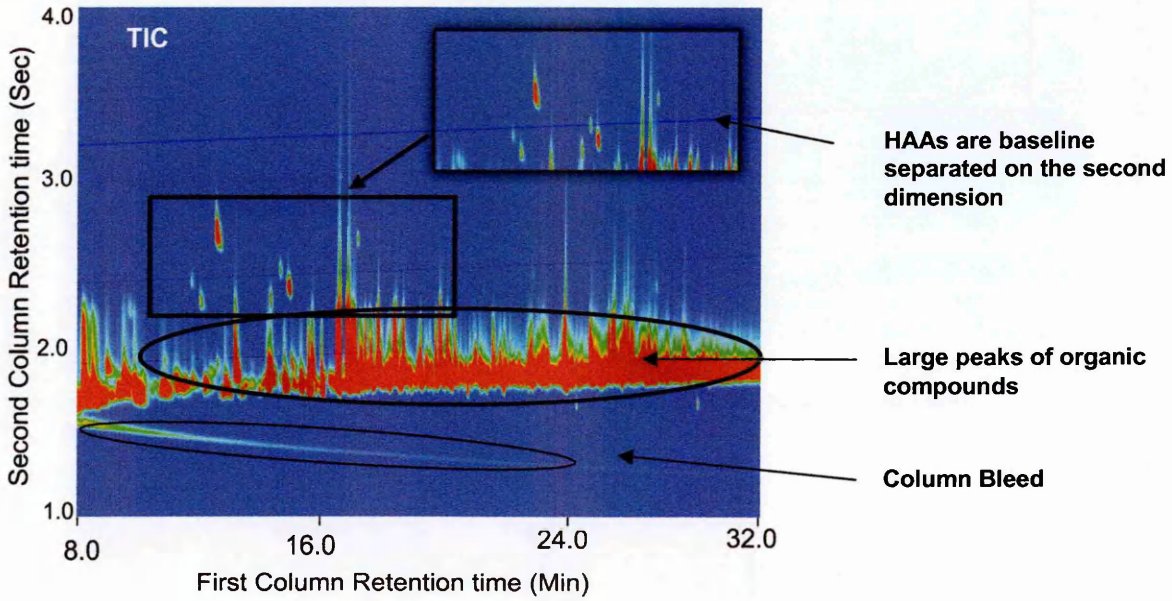
Given the issues identified with resolving HAAs from matrix peaks using traditional GC-MS, it was decided to investigate the potential benefit of the orthogonal resolving power possible through multi-dimensional gas chromatography.

Derivatised HAAs standards were analysed on a Leco Pegasus GC×GC-time of flight mass spectrometer (GC×GC-ToFMS). The orthogonal separation provided by comprehensive chromatography was obtained by using an Agilent 6890 GC fitted with a thermal modulator (Zoex UK Ltd), coupled to a Pegasus IV time-of-flight mass spectrometer (Leco Corporation Inc.). Such an instrument has not been reported as being used for the analysis of HAAs before. The instrument parameters used for the analyses are described in Section 3.2.4.

Total ion chromatograms for a derivatised HAA9 calibration standard (100 µg/l) and a procedural blank (0 µg/l) are shown in Figure 5.12 and Figure 5.13 respectively. Figures A) display the chromatograms in contour mode (2D plot), whilst B) display surface plots in 3D relief. The chromatograms showed the presence of several hundred organic compounds within both the standards and blanks. From comparison of the fragmentation patterns with the NIST library, we were able to determine that the interference peaks at high levels were found to be derivatives of haptane, haptene, propane and propene. The intensity of these peaks dwarfed the derivatised HAA peaks within the standards. The column configuration incorporating a relatively non-polar (SGE BPX5) and a mid-polar (SGE BPX50) separated the HAAs from the compounds that co-eluted on one column. As

can be seen, the GC×GC was very efficient at separating the HAAs from these matrix interferences.

A



B

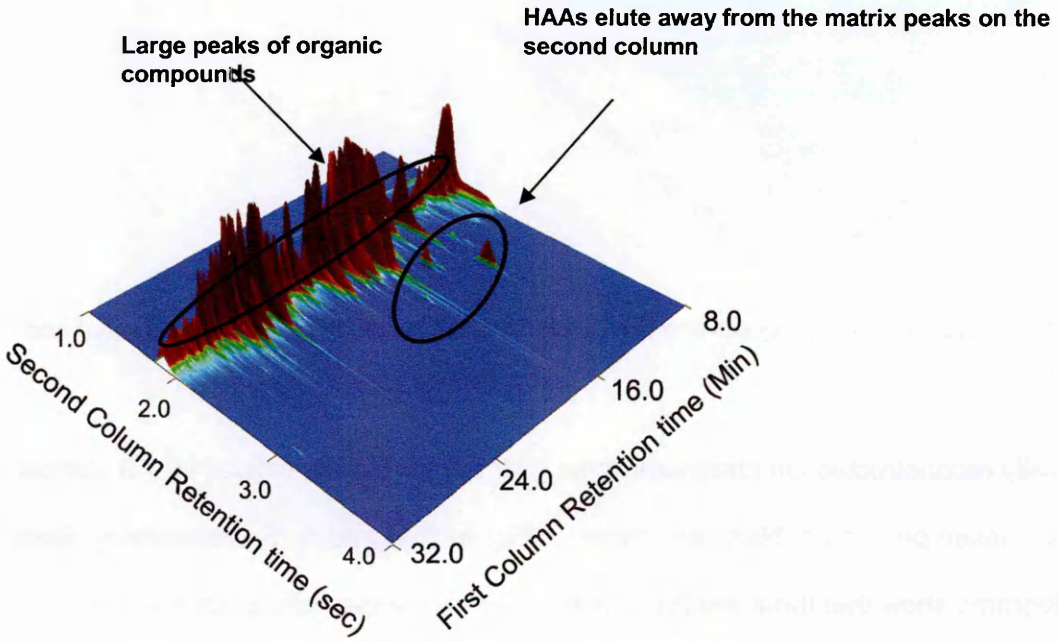
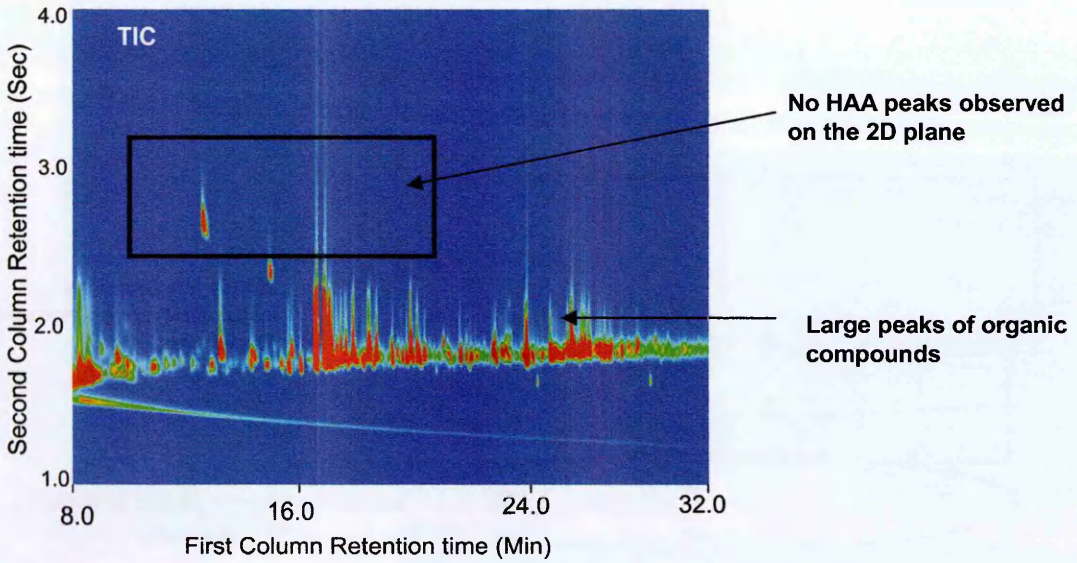


Figure 5.12: A total ion chromatogram of a derivatised HAA9 standard (100 µg/l) in A) contour and B) 3D relief. The retention times of the HAAs were between 9 - 24 min on the 1st column and 2 - 3 seconds on the 2nd column. Insert: expanded between 9 - 20 min on 1st column and 2.2 - 3 seconds on the 2nd column.

A



B

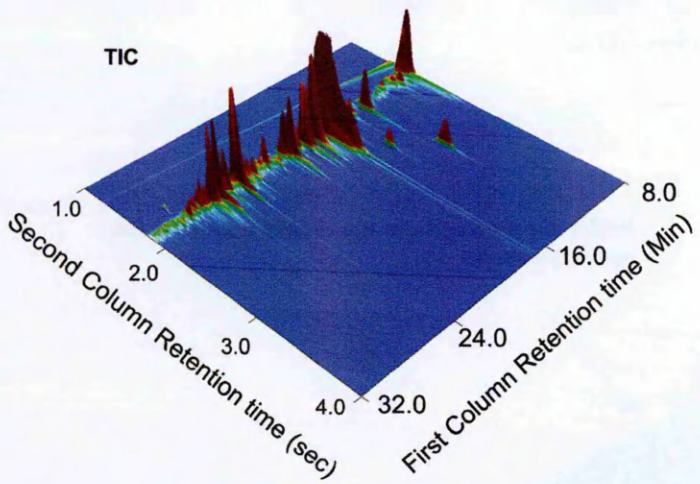


Figure 5.13: A total ion chromatogram of a derivatised procedural blank (0 µg/l) in A) contour and B) 3D relief.

The partially reconstructed ion chromatograms (*m/z* 59) for the derivatised HAA9 standard and a derivatised procedural blank are shown in Figure 5.14 and 5.15, respectively. Both chromatograms show that there are much fewer organic compounds containing the fragment ion, *m/z* 59. The intensity of these interfering peaks, therefore, was greatly reduced, providing better specificity and selectivity for the HAAs. The partially reconstructed chromatogram (*m/z* 59) of the procedural blank does not indicate the presence of any peaks in the region that HAAs would be present.

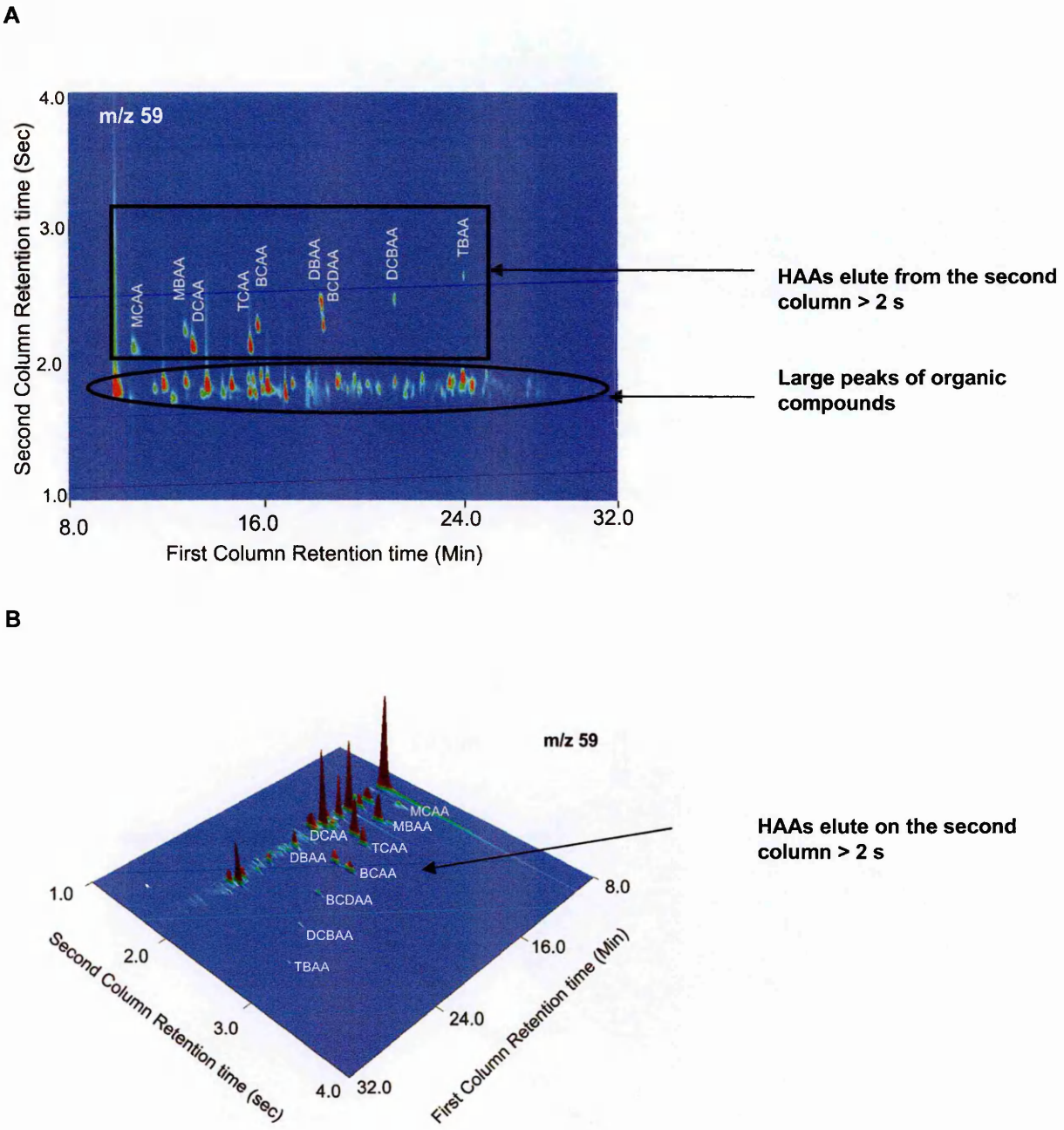
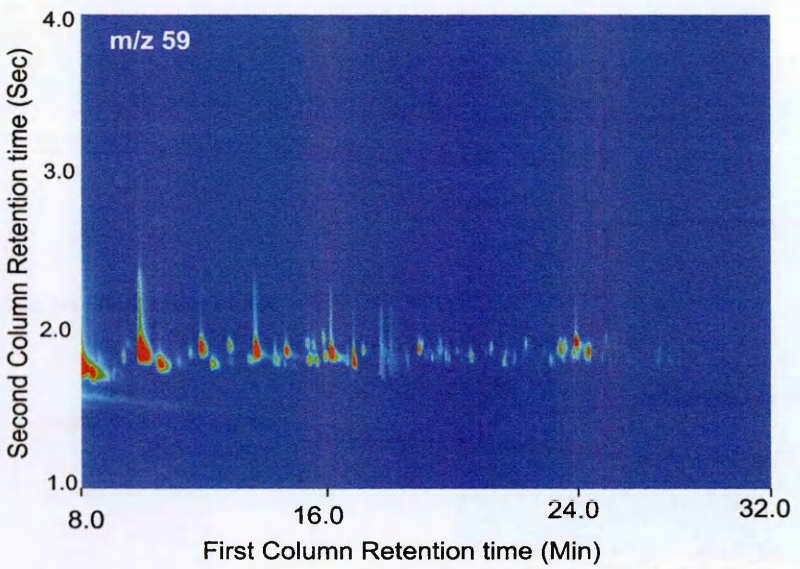


Figure 5.14: A partially reconstructed ion chromatogram (m/z 59) of a derivatised HAA9 standard (100 µg/l) in A) contour and B) 3D relief. The retention times of interest for HAAs were 9 - 24 min on the 1st column and 2 – 3 seconds on the 2nd column.

A



B

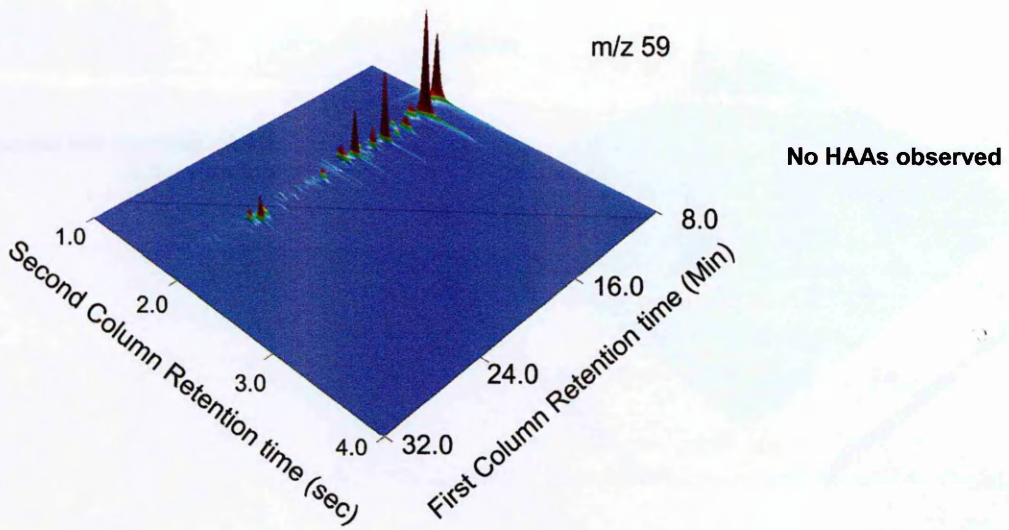


Figure 5.15: A partially reconstructed ion chromatogram (m/z 59), of a derivatised procedural blank (0 µg/l) in A) 3D relief and B) contour. No peaks are found at the appropriate retention times in the region of interest for the HAAs.

Determining the linearity, repeatability, accuracy and LOD for each HAA species

These studies on the GC×GC-ToFMS were determined utilising the parameters based on that described in Section 5.3.2.4. In this study, the repeatability and accuracy was evaluated using five injections of a 50 µg/l derivatised HAA9 standard, while the linearity studies used a single injection of each calibration standard. The LOD was calculated on 7 replicate analyses of a derivatised standard at 1 µg/l.

The results, as summarised in Table 5.9, showed that the correlation coefficients (R^2) for each of the HAAs were better than 0.9856 over the concentration range of 1 - 100 µg/l. The HAA peak areas had a repeatability of 1.6 - 7.7 %, for the 50 µg/l standard, while the repeatability of the 1 µg/l standard was higher, from 11.7 - 19.9 % for 8 of the HAAs, with the exception of TBAA which was at 21.4 %. The accuracy of the HAAs, at 50 µg/l, was found to be between 97.8 - 112.1%, while the accuracy at 1 µg/l was 77.2 - 125.8 %. These results were within the acceptable recoveries (accuracy) and precision of ± 20% for the mid range standard (50 µg/l) required by USEPA Method 552.3 (2003). The detection limit study showed that MCAA was the highest at 0.79 µg/l, whilst MBAA was found to have the lowest at 0.38 µg/l.

Table 5.9: The mean 1st and 2nd column retention times, linear correlation coefficients, accuracy, repeatability, LODs and MRLs for each of the nine HAAs, as obtained using the GC×GC-ToFMS.

Compound	1st column retention time (Min)	2nd column retention time (Sec)	Quantitation ion (*m/z*)	Correlation coefficient [1] (R^2)	Accuracy [2] (%)		Repeatability RSD [3] (%)		LOD [4] (µg/l)	MRL [5] (µg/l)
					1 µg/l *n=7*	50 µg/l *n=5*	1 µg/l *n=7*	50 µg/l *n=5*	1 µg/l *n=7*	*n=7*
MCAA	9.69	2.02	59	0.9878	125.8	102.3	19.93	7.70	0.789	2.37
MBAA	11.84	2.11	59	0.9868	95.2	106.8	12.68	5.50	0.380	1.14
DCAA	12.19	2.05	59	0.9991	107.3	103.6	19.27	3.98	0.651	1.95
TCAA	14.63	2.06	59	0.9954	105.5	107.7	12.68	2.09	0.421	1.26
BCAA	14.99	2.19	59	0.9990	84.7	100.8	19.37	4.56	0.516	1.55
DBAA	17.66	2.36	59	0.9998	95.3	109.9	18.65	4.90	0.560	1.68
BDCAA	17.75	2.25	59	0.9921	77.4	112.1	11.70	1.57	0.599	1.80
DBCAA	20.85	2.38	59	0.9860	82.2	97.8	14.21	7.03	0.476	1.43
TBAA	23.84	2.55	59	0.9856	82.7	106.0	21.35	2.67	0.555	1.67
IS	15.26	2.13	75	-	-	-	-	-	-	-

[1] *The linear range for 1 - 100 µg/l of derivatised HAA9 standards,*

[2] *The accuracy of 1 µg/l (n=7) and 50 µg/l (n=5) derivatised HAA9 standard,*

[3] *The repeatability (precision) of 1 µg/l (n=7) and 50 µg/l (n=5) HAA9 derivatised standard,*

[4] *The LOD was derived from a 1 µg/l derivatised HAA9 analytical standard (n=7),*

[5] *The MRL calculated at 3 times LOD.*

5.3.5 The analysis of HAAs using GC-MS in chemical ionisation mode

Chemical ionisation (CI) is a lower energy alternative to electron impact and can be used in both positive (PCI) and negative (NCI) modes. It uses a reagent gas to reduce the electron energy from around 70 eV to <10 eV, which in turn can reduce compound fragmentation, preserving the structure and producing simpler mass spectra. The NCI ionisation mode has been reported to provide a higher response for halogenated compounds (Hübschmann, 2009). Therefore the potential of CI for the analyses of HAAs was investigated on an Agilent 7860-5975C quadrupole GC-MS.

At the start of this study, a brief overview of the literature was performed to explore whether GC-MS in CI mode had been used for the analysis of HAAs in drinking water. As no study was found, a set of baseline CI parameters was selected, and derivatised HAA9 standards (100 µg/l) were analysed in NCI mode in full scan mode (*m/z* 30 – 350).

Visual inspection of the resulting TIC chromatogram is shown in Figure 5.16. On further investigation, the ions, *m/z* 35 $[Cl]^-$ and 81 $[Br]^-$, were found to be the most abundant fragment ions in the TIC. Several unknown peaks were observed in the chromatogram, but they did not interfere with the HAAs and IS. As can be seen, DBAA and BDCAA were slightly unresolved.

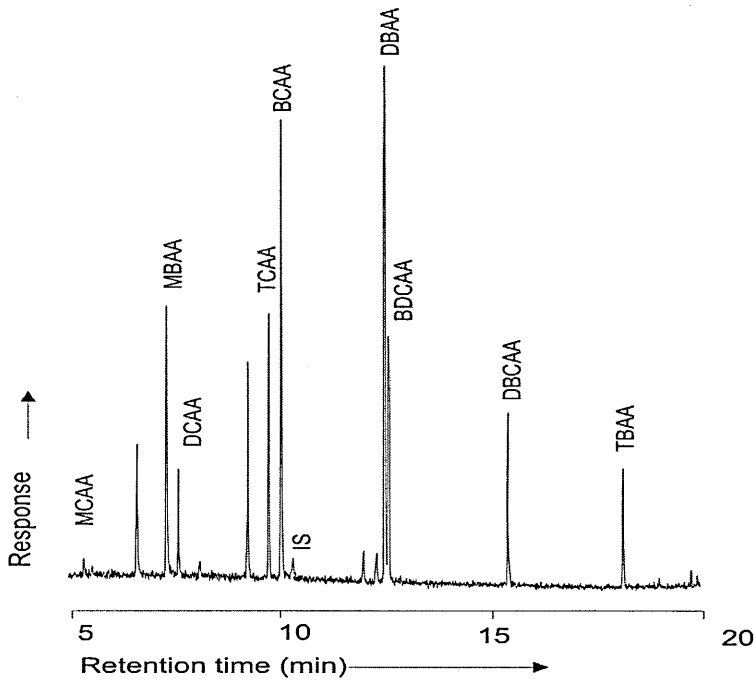


Figure 5.16: TIC chromatogram obtained by GC-MS (ECNI), showing the response of a derivatised HAA9 standard (100 µg/l) and IS (1000 µg/l).

Generally, NCI involves an ion/molecule reaction either to add an anion to a gas-phase analyte molecule or to abstract a proton from the analyte molecule. In addition, under the same conditions as NCI, electron capture negative ionisation (ECNI) is also possible (Watson *et al.*, 2008). ECNI does not involve an ion/molecule reaction, instead it involves the direct interaction of the analyte molecule with a thermal electron (0 - 15 eV) generating negative ions. This is most likely to take place by dissociative electron capture, as shown in Equation 5.2 (Watson *et al.*, 2008)

$$AB + e^- (0 - 15\ eV) \rightarrow A + B^- \qquad \text{Equation 5.2}$$

It may also be possible that ion pair formation is also taking place, as shown in Equation 5.3 (Watson *et al.*, 2008)

$$AB + e^- (> 10\ eV) \rightarrow A^+ + B^- + e^- \qquad \text{Equation 5.3}$$

Method optimisation

The influence of CI parameters on the response of HAAs was investigated to optimise the original method. Switching the chemical ionisation gas from methane to isobutane, resulted in better responses, which were believed to arise from it being more efficient at converting the electrons into the energy range that promotes dissociative electron capture. This was because isobutane was a 'softer' reagent gas with higher proton affinity than that of methane.

Having identified that the base fragment ions of interest for the HAAs were *m/z* 35 and 81, derivatised HAA9 standard (100 µg/l) and IS (1000 µg/l) were run in selected ion monitoring (SIM) mode. The resulting chromatogram (combined *m/z* 35 + 81) is shown in Figure 5.17. The chromatogram shows good peak sensitivity for all the HAAs and IS. There were a few unknown peaks but they did not interfere with any of the HAAs and IS. As can be seen, DBAA and BDCAA were baseline resolved.

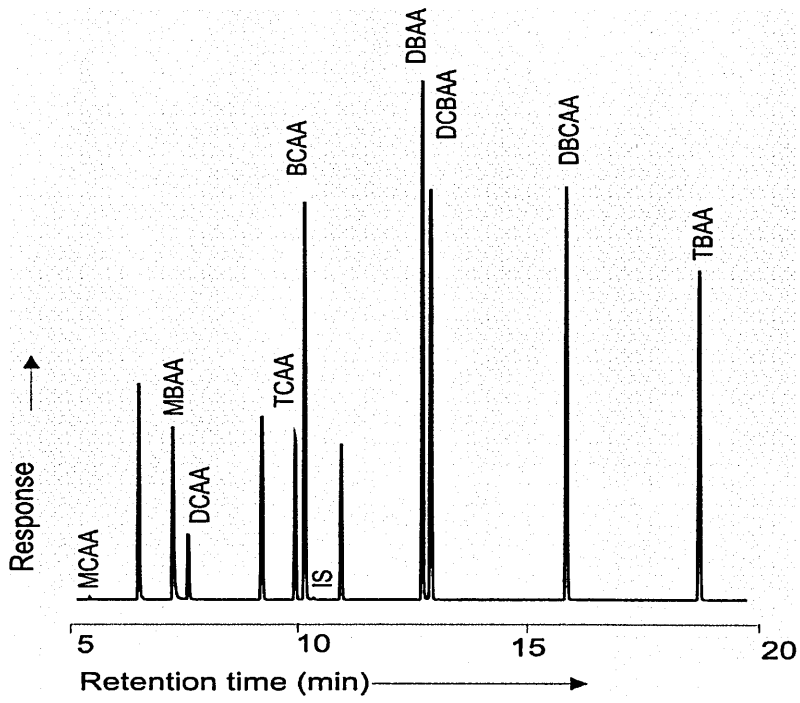


Figure 5.17: SIM chromatogram obtained by GC-MS (ECNI) of a derivatised HAA9 standard at 100 µg/l of each compound and 1000 µg/l IS. SIM ions m/z 35 and 81.

The quantitation of HAAs was performed using the base fragment ions *m/z* 35 and *m/z* 81. Partially reconstructed ion chromatograms (RIC) for each ion, are presented in Figure 5.18.

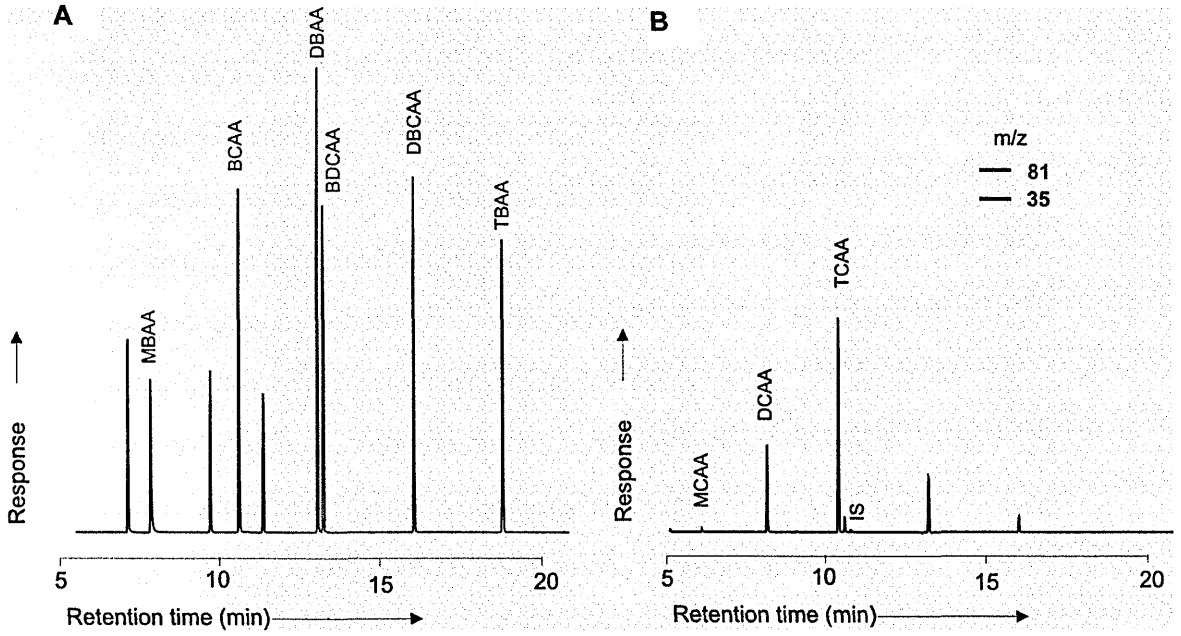


Figure 5.18: Partially reconstructed ion chromatograms (RIC) of a derivatised HAA9 standard (100 µg/l) and IS (1000 µg/l) using fragment ion A) m/z 81 and B) m/z 35, obtained by GC-MS in ECNI mode.

The *m/z* 35 ion was used for the chlorine containing HAAs such as MCAA, DCAA, TCAA and the IS (1,2,3 trichloropropane). The *m/z* 81 ion was used for the six bromine containing HAAs, namely: MBAA, BCAA, DBAA, BDCAA, DBCAA and TBAA. The s/n ratios of the HAAs from the chromatograms are reported in Table 5.10.

Table 5.10: The signal to noise ratios of the nine HAAs obtained by GC-MS in ECNI.

	MCAA	MBAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA	IS
RIC	123	5429	3081	7739	12224	16573	11642	12847	10450	118

Other parameters, such as reagent gas flow rate, were also optimised and the final parameters have been reported in Section 3.2.4.5. These conditions were then used for determining the linearity, repeatability, accuracy and LOD of each HAA.

Determining the linearity, repeatability, accuracy and LOD

These studies utilised the methodology previously reported in Section 5.3.1.4 except that the repeatability was performed on seven replicate injections of a derivatised HAA9 (50 µg/l) and the detection limits were determined using seven replicate injections of a derivatised HAA9 standard at 2 µg/l.

The results of the linearity studies are shown in Figure 5.19. The correlation coefficients (R^2) for each HAA are better than 0.9859 (Table 5.11).

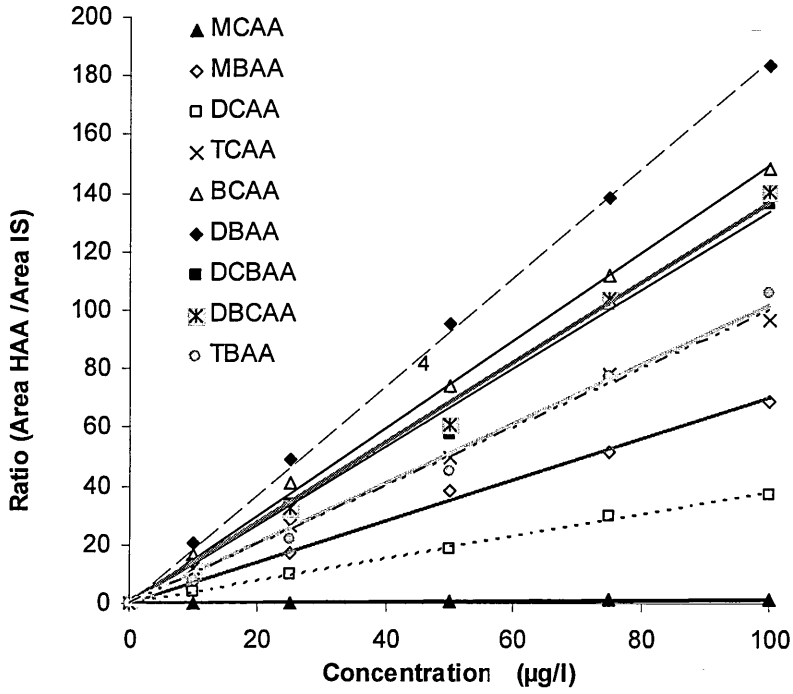


Figure 5.19: The linear calibration plots for the nine HAAs obtained by GC-MS (ECNI).

The results, as reported in Table 5.11, showed that the LOD for each species was found to be in the range 0.4 - 1.5 µg/l. The accuracy of the measurement were found to be between 86.9 - 112.5 % and 90.5 - 111.6 % for the 50 µg/l and 5 µg/l standards, respectively. The repeatability was between 2.4 - 7.6 % for the 50 µg/l standard and 11.4 - 15.6 % for the 5 µg/l standard. These results are comparable to the USEPA 552.3 method which reported an accuracy of 98.2 - 111 % for a 10 µg/l derivatised HAA9 standard and an accuracy of 92.2 - 128 % for the 1 µg/l standard. They were within the acceptable analyte recoveries of ± 20 % at the mid-range standard of the calibration curve (USEPA 552.3, 2003).

Table 5.11: The mean retention times, linearity correlation coefficients, accuracy, repeatability, LODs and MRLs of nine HAAs obtained using the GC-MS (ECNI).

Compound	Mean retention time (min)	Correlation coefficient [1] (R^2)	Accuracy [2] (%)		Repeatability RSD [3] (%)		LOD [4] (µg/l)	MRL [5] (µg/l)
			5 µg/l *n*=7	50 µg/l *n*=7	5 µg/l *n*=7	50 µg/l *n*=7	*n*=7	*n*=7
MCAA	5.51	0.9859	86.9	90.5	11.35	7.63	1.475	4.42
MBAA	7.47	0.9993	103.9	108.9	11.42	5.17	0.902	2.71
DCAA	7.77	0.9975	102.0	105.5	15.52	3.93	0.727	2.18
TCAA	10.08	0.9945	110.5	109.1	15.03	2.43	0.409	1.23
BCAA	10.44	0.9975	109.6	109.9	11.64	2.75	0.940	2.82
DBAA	13.08	0.9899	112.5	101.2	12.61	3.64	1.074	3.22
BDCAA	13.15	0.9955	100.9	106.2	13.12	3.63	0.963	2.89
DBCAA	16.20	0.9955	92.0	98.4	12.55	4.79	0.756	2.27
TBAA	19.18	0.9875	109.9	111.6	12.34	6.91	1.259	3.78
IS	10.71	-	-	-	-	-	-	-

[1] *The linear range for 1 - 100 µg/l of derivatised HAA9 standards,*

[2] *The accuracy of 50 µg/l derivatised HAA9 analytical standard (n = 7),*

[3] *The repeatability of 50 µg/l HAA9 derivatised analytical standard (n = 7),*

[4] *The LOD was derived from 2 µg/l derivatised HAA9 analytical standard (n = 7),*

[5] *The MRL was calculated at 3 times the LOD (n = 7).*

5.4 Discussion of the methods investigated

HAAs are currently not regulated in the UK, but are considered a high priority compound for future regulations (Fawell *et al.*, 2002). GC-μECD is the established instrumentation used for the analysis of HAAs (Malliarou *et al.*, 2005; Pepich *et al.*, 2004; Qi *et al.*, 2004; Rodriguez *et al.*, 2004; USEPA, 1990; USEPA, 1992; USEPA, 2003a; Villanueva *et al.*, 2003; Yang *et al.*, 2005). Prior to analysis, the HAAs must be extracted and derivatised making the method time consuming and expensive (Harman *et al.*, 2011).

Owing to the selective nature of the GC-μECD, the instrument is known for its linearity, repeatability, accuracy and sensitivity. Despite these analytical characteristics, the use of GC-μECD is not without its drawbacks, as reported earlier. In addition, the selection of the most appropriate stationary phase for the GC column has been shown to be important to prevent the overestimation of the concentration of certain HAAs (DCAA) in treated water samples. This chapter has evaluated alternative chromatographic and detection methods for the analysis of HAA standards and includes a comparison of the performances of GC-μECD, GC-MS (EI), GC×GC-ToFMS and GC-MS (ECNI). Their performance, relative to the GC-μECD method (developed for this study) and USEPA Method 552.3, has been reported in Table 5.12.

In this study, the HAAs could not be uniquely identified by the GC-MS (EI), in either full scan or SIM modes. This is believed to be owing to the presence of hundreds of interfering compounds present within the standards and procedural blanks (as later confirmed by the GC×GC-ToFMS data). This result was unexpected as GC-MS (EI) has previously been reported for the analysis of derivatised HAAs (Sadia *et al.*, 2009; Scott *et al.*, 1998; Xie, 2001). Xie (2001) developed a liquid-liquid extraction-GC-MS (SIM) method for the analyses of nine HAAs and dalapon, with LODs less than 1 μg/l and recoveries of 73 to 165 %. Further work needs to be performed to investigate the source of these compounds which prevented the separation and resolution of the HAAs.

This study has also shown the importance of using suitable capillary columns for the accurate measurement of HAA concentrations in treated water samples. The GC×GC-ToFMS proved to be a powerful instrument for the analysis of all nine derivatised HAAs with suitable LOD, accuracies and recoveries, as shown in Table 5.12. The fragmentation patterns of the HAAs were matched to a library database (>70 %) and retention times were referenced to analytical standards. The instrument's deconvolution algorithm was also instrumental in the separation and detection of co-eluting compounds (used again in Chapter 6). However from a practical perspective, the instrument required longer analysis and data processing times, and the data analysis can be labour-intensive. The higher initial instrument cost and higher maintenance costs, because of the regular use of liquid nitrogen, would likely prevent its wide-scale application in industry. As the instrument was easily available to the author for this research, some of these disadvantages were not of concern. However, alternative comprehensive chromatography techniques are becoming increasingly available and affordable which would allow such analyses to become routine. The use of capillary flow technology (CFT) is driving these developments and should be explored further.

In this study, the GC-MS (ECNI) proved to be capable for the detecting and quantifying HAAs. The use of characteristic fragment ions (*m/z* 35 and *m/z* 81 for Cl^- and Br^-, respectively) for quantitation and the use of isobutane reagent gas further improved the response. The analytical accuracy and precision were higher but generally suitable, as reported in Table 5.12. The main disadvantages of ECNI analyses were: there were no standard libraries for identifying spectral peaks against reference standards; the possibility of peak co-elution of the HAAs and the inability to detect specific HAAs (such as MCAA) at the concentration required. This method requires further optimisation to improve its analytical performance to the levels required to compete with the GC-μECD.

The other methods developed showed comparable linearity, repeatability and accuracy to those reported and required for USEPA Method 552.3, as summarised in Table 5.12.

Table 5.12: Overview of the sample preparation, analysis time, linearity, repeatability, accuracy, LODs and MRLs of methods investigated for the analysis of HAAs in this study, compared to the USEPA Method 552.3.

Instrument	Sample Preparation	Analysis Time	Linearity (R^2)	Repeatability (%)	Accuracy (%)	LOD (µg/l)	MRL (µg/l)	Suitability
GC-µECD [1]		< 35 min	0.9890 - 0.9989	1.7 - 4.6 (100 µg/l) 1.3 - 4.2 (50 µg/l) 1.1 - 4.3 (1 µg/l)	93.2 - 106.3 (100 µg/l) 89.3 - 109.3 (50 µg/l) 75.7 - 129.5 (1 µg/l)	0.07 - 0.28 HAA5 < 0.87 HAA9 < 1.30	0.15 - 0.83	Yes
GCxGC-ToFMS		< 45 min	0.9856 - 0.9998	1.6 - 7.7 (50 µg/l 11.7 - 21.4 (1 µg/l)	97.8 - 112.1 (50 µg/l) 77.2 - 125.8 (1 µg/l)	0.38 - 0.79 HAA5 < 2.81 HAA9 < 4.95	1.14 - 2.37	Yes
GC-MS (EI)	Extensive 6 hour sample preparation required	< 45 min	n/r	n/r	n/r	n/r	n/r	No [2]
GC-MS (ECNI)		< 35 min	0.9875 - 0.9993	2.4 - 7.6 (50 µg/l) 11.4 - 15.6 (5 µg/l)	86.9 - 112.5 (50 µg/l) 90.5 - 111.6 (5 µg/l)	0.41 – 1.48 HAA5 < 4.59 HAA9 < 8.51	1.23 - 4.42	Yes [3]
USEPA 552.3 GC-µECD [1]		< 45 min	n/r	0.5 – 4.7 (10 µg/l) 0.4 - 4.1 (1 µg/l)	98.2 - 113 (10 µg/l) 92.2 - 128 (1 µg/l)	0.01 - 0.17 HAA5 < 0.25 HAA9 < 0.46	0.03 - 0.51	
USEPA Recommendations		n/a	n/a	± 20 % [4]	± 30 % [4]		1 – 4 [5]	
IC [6]	< 10 min	< 55 min	0.9644 – 0.9997	n/r	n/r	2.6 - 31.9	n/r	No

[1] *Analysis on a J&W DB 5.625 column,*
[2] *Reported by Xie (2001) but not appropriately resolved and quantified in this study,*
[3] *Shown good potential but further work needs to be done to improve its performance,*
[4] *Recommended by US EPA Method 552.3 (2003),*
[5] *Recommended Minimum Reporting Levels (MRL) for the 9 HAAs as reported by USEPA DBP/ICR Analytical Methods Manual (1996),*
[6] *Investigated at Cranfield University and concluded to be unsuitable because of high detection limits (Bougeard, 2009).*
n/r – not reported, n/a not applicable

The biggest discriminator between the methods was the LOD (MRL) values determined for each HAA. A comparison of the LODs, for individual HAAs, for each of the analytical instrument methods investigated in this study, is provided in Table 5.13, along with representative LODs reported in the literature.

The results showed that the detection limits of the HAAs on the GC-μECD were higher than those reported by USEPA 552.3, but similar to those reported in USEPA 552.2 (1995). Malliarou *et al.* (2005) reported detection limits for six HAAs, which were much higher (up to 6.2 times) than the GC-μECD results in this study (No LODs were reported for MCAA, DBCAA and TBAA in their study). Rodriguez *et al.* (2004) also reported higher detection limits. A comparison of the HAA detection limits on the three instruments used in this study confirmed that the LODs from the GC×GC-ToFMS were higher than those obtained by the GC-μECD, while the GC-MS (ECNI) had the highest detection limits for the HAAs.

The general minimum reporting levels (MRL) suggested by USEPA in the DBP/Information Collection Rule Analytical Methods Manual (USEPA, 1996a) are also listed in Table 5.13. Apart from the GC-μECD, the GC×GC-ToFMS and GC-MS (ECNI) results reported higher MRL's to those recommended by the USEPA Methods. However, having achieved the primary aim of this study, *i.e.* to explore the suitability of alternative instruments for the accurate and reliable analysis of HAAs, further optimisation studies on these instruments could be conducted which might further improve their LODs and MRLs to the required levels.

Table 5.13: Comparison of the LODs on the analytical instrument investigated in this study with those reported in literature.

Compound	LOD (µg/l)				MRL (µg/l)	LOD (MRL) (µg/l)					
	USEPA 552.2 (1995b) [1]	USEPA 552.3 (2003) [1]	Rodriguez *et al.*, (2004) [1]	Malliarou *et al.*, (2005) [1]	USEPA (1996) [2]	GC-µECD		GC×GC-ToFMS		GC-MS (ENCI)	
MCAA	0.27	0.17	1.2	n/r	2	0.277	(0.83)	0.789	(2.37)	1.475	(4.42)
MBAA	0.20	0.03	0.9	0.40	1	0.187	(0.56)	0.380	(1.14)	0.902	(2.71)
DCAA	0.24	0.02	1.1	0.80	1	0.087	(0.26)	0.651	(1.95)	0.727	(2.18)
TCAA	0.08	0.02	0.6	0.70	1	0.159	(0.48)	0.421	(1.26)	0.409	(1.23)
BCAA	0.25	0.02	0.9	1.30	1	0.069	(0.21)	0.516	(1.55)	0.940	(2.82)
DBAA	0.07	0.01	1.3	0.40	1	0.157	(0.47)	0.560	(1.68)	1.074	(3.22)
BDCAA	0.09	0.05	n/r	1.30	1	0.078	(0.23)	0.599	(1.80)	0.963	(2.89)
DBCAA	0.47	0.03	n/r	n/r	2	0.049	(0.15)	0.476	(1.43)	0.756	(2.27)
TBAA	0.82	0.11	n/r	n/r	4	0.236	(0.71)	0.555	(1.67)	1.259	(3.78)
HAA5	0.86	0.25	5.10	2.30	6.0	0.87		2.80		4.59	
HAA9	2.49	0.46	-	(4.9)	14.0	1.30		4.95		8.51	

[1] Analyses performed on the GC-µECD, [2] Minimum Reporting Level (MRL) recommended by the USEPA DBP/ICR Analytical Methods Manual (1996).

MCAA was found to have the highest detection limits in all methods. Other have also reported higher LODs for MCAA whilst some studies have not been able to measure MCAA, reporting analytical errors on the GC-μECD (Malliarou *et al.*, 2005; Reckhow *et al.*, 2008; Xie, 2001).

A review was performed to assess the range of MCAA concentrations reported across the UK and other countries. Graham *et al.,* found that the concentration of MCAA was below detection levels in three drinking water supply systems (upland surface water, a lowland surface water, and a groundwater) in England (Graham *et al.*, 2009). However, MCAA concentrations have been reported in several other studies in countries such as Australia, Poland, China, USA and Canada (Dmitruk *et al.*, 2007; LeBel *et al.*, 1997; Simpson *et al.*, 1998; Williams *et al.*, 1997; Zhou *et al.*, 2004). Apart from the Australian waters, where MCAA was found at 10 μg/l - 244 μg/l (Simpson *et al.*, 1998), all the other studies reported levels for MCAA below 10 μg/l. Although MCAA is a USEPA regulated HAA, their levels in the UK, and to a greater extent the global studies investigated, would suggest that their measurement should not be a major driver for higher instrument sensitivity.

5.5 Conclusion

In summary, the optimised GC-μECD was the simplest and most sensitive method with slightly superior analytical accuracy and repeatability, to the GC×GC-ToFMS. Both systems had suitable levels of linearity, accuracy and repeatability. The GC×GC-ToFMS was also found to be a reliable instrument for the analyses of HAAs providing selectivity, compound identification and a reduction in interferences. Therefore, the GC-μECD and GC×GC-ToFMS were used for evaluating the formation potentials of the individual HAAs in Chapter 6 and the optimised GC-μECD method was used for the geographic study of the HAA concentrations present in water samples from around the UK, as reported in Chapter 7.

6. A study measuring the formation potential of THMs and HAAs in treated UK waters

The preliminary findings of this work have been published in the Chapter 7 of the book, *Disinfection By-Products in Drinking Water: Occurrence, Formation, Health Effects, and Control* from American Chemical Society Symposium Series 995 (Bougeard *et al.,* 2008) and can be found in Appendix 4. The results reported in the book chapter were based on the analytical work done on the GC-μECD, prior to the knowledge of the co-elution and overestimation of the DCAA concentrations as reported in this Chapter.

6.1 General Introduction

Disinfection is a vital process in the treatment of drinking water to prevent the spread of water-borne diseases. However, this process leads to the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs).

There are four THMs (THM4) which are regulated in the UK at a total concentration of 100 μg/l (DWI, 2000). Five of the nine HAAs are regulated in the US at a total concentration of 60 μg/l. HAAs are currently not regulated in the UK and Europe, but are considered for potential regulation (Cortvriend, 2008). HAAs have been found in drinking water across the UK, with mean HAA9 concentrations between 35 μg/l to 95 μg/l, with a maximum total HAA concentration of 244 μg/l (Malliarou *et al.*, 2005).

The primary factors that influence the formation potential of HAAs and THMs are pH, temperature, bromide concentration in the water, natural organic matter (NOM) composition and concentrations, the type of disinfection agent (such as chlorination or chloramination), the disinfection contact time and the disinfection agent concentration

(Dojlido *et al.*, 1999; Krasner *et al.*, 1989; Krasner *et al.*, 1996; Liang *et al.*, 2003; Nikolaou *et al.*, 2004b; Qi *et al.*, 2004; Reckhow *et al.*, 2008; Sharp *et al.*, 2006; Westerhoff, 2006).

With minimal information available on the distribution of HAAs in UK drinking water, a study was undertaken to characterise the formation potential of THMs and HAAs produced by the chlorination of geographically different sources of water. The aim of this study was to:

1. Determine the influence of various disinfection parameters on the formation of THMs and HAAs, under controlled laboratory conditions, to establish whether UK treated waters follow the trends reported in other countries. The following parameters: contact time, pH, temperature, and bromide concentrations, during chlorination were investigated.
2. Evaluate if THM concentrations could be used as a surrogate for HAA concentrations in UK waters. Given the complexity and time required to establish HAA concentrations, the validity of any relationship between the formation of THM and HAA at different pH bromide concentrations and temperature was also investigated.
3. Evaluate the suitability of two analytical methods (GC-μECD and GC×GC-ToFMS), optimised in Chapter 5, for the measurement of HAA concentrations in real water samples. The use of comprehensive chromatography for the analysis of HAAs has previously not been reported in literature.

This study was funded by several water companies across the UK and performed collaboratively by members of Cranfield University and The Open University. The initial sampling, sample preparation and sample derivatisation were performed at Cranfield University, whilst the instrument optimisations, sample analyses and concentration determinations were conducted primarily by the author at The Open University.

6.2 Materials and experimental analyses

6.2.1 Bulk water sample collection and storage

Water samples were collected, in June 2006, from both lowland and upland drinking water treatment works in clean plastic containers (~ 250 l each). The samples were obtained after the respective water treatment processes but before disinfection. The sampling points within the process flow of the two water treatment works (WTW) are shown in a schematic in Appendix 3. The treated water samples were returned to the laboratory at Cranfield Water Science Institute, at Cranfield University and stored in clean plastic containers (~ 25 l), at 5 °C, and were labelled as bulk water.

The lowland water reservoir was situated on a plateau where the water was extracted from a local river in South East England, whilst the upland water reservoir contained water from peat-rich moorlands in northern England.

The sample preparation was performed between January and March 2007, at Cranfield University, and brought over to The Open University for analysis between January and April 2007. Parameters such as pH, bromide content, UV absorbance and the alkalinity of each of the two water sources were measured at Cranfield University. All the calibration standards and materials used in this chapter have been previously reported in Chapter 3.

6.2.2 Method for measuring the 7-day formation potentials of THMs and HAAs in bulk water

Formation potential experiments are run to determine the potential of selected water to form disinfection by-products under a standard or a user-specified set of reaction conditions. The experiments were conducted using an adapted version of Procedure 5710, from 'Standard Methods for the Examination of Water and Wastewater' (Greenberg, 1992).

A 100 ml glass bottle was part filled with the water from the required water source. It was buffered to pH 7 by the addition of phosphate buffers (0.07 M sodium phosphate dibasic (Na_2HPO_4) and 0.07 M potassium phosphate monobasic (KH_2PO_4)). An appropriate volume of standardised stock sodium hypochlorite solution was added to the water to obtain the chlorine dose of 5 mg/l. The bottle was filled up to the top with the same water sample and capped with a PTFE-lined cap ensuring there was no headspace. This was performed in duplicate and the samples were incubated for 168 hours (7 days), in the dark, at 20 °C. A free-chlorine residual was maintained at ≥ 1 mg/l as Cl_2 after seven days (168 hours) of contact time (the free chlorine is the excess chlorine present in treated waters for the purposes of inactivating disease-causing micro-organisms). The samples were then quenched with 0.1 ml of 100 mg/ml sodium sulphite solution, as used in USEPA Method 552.3, to remove any residual chlorine and to stop any further chlorination (USEPA, 2003a).

The procedures for the preparation of the sodium sulphite solution and the fortnightly measurement of the sodium hypochlorite concentrations are reported in Appendix 3.

6.2.3 Investigating the influence of various parameters on the formation potential

In addition to evaluating the 7-day formation potential at pH 7, the kinetics for the formation of THMs and HAAs were investigated by varying the contact time between 0.5 and 168 hours. The concentration measurement for THMs and HAAs were performed on the two water sources after contact times of 0, 0.5, 1, 3, 6, 12, 24, 72 and 168 hours.

The influence of pH on the formation potential of the two water sources was investigated by repeating the above experiments at a pH of 6 and 8 (rather than pH 7). This pH range was investigated because such variation can be expected to occur in natural water samples in the UK.

The influence of bromide ions on the formation potential of the water sources was investigated by spiking the water samples with bromide ions at a concentration of 200 µg/l. Elevated concentrations of bromide ions can be found occurring naturally in real waters and are known to fluctuate seasonally and geographically.

The influence of reducing the temperature during chlorination was also investigated by incubating the samples at a temperature of 7 °C (rather than 20 °C). The known diurnal and seasonal temperature variations, such as those reported in Chapter 2, prompted the need to investigate the influence of temperature.

6.2.4 The methods for analysis of THMs and HAAs present in the quenched water samples generated by formation potential experiments

THM analyses

30 ml of the quenched water sample was transferred to a 30 ml glass vial and refrigerated at 4 °C, without a headspace. Using an automatic pipette, 5 ml of the water was pipetted into a 10 ml vial allowing 5 ml of headspace. The vial was then immediately capped. Analyses were performed using headspace-gas chromatograph-mass spectrometry (HS-GC-MS), within a week of the original transfer. The details of the instrument parameters utilised have been reported in Chapter 3.

HAA analyses

30 ml of the quenched water sample was transferred to a 50 ml glass bottle. The HAAs in the water were extracted and derivatised to their respective methyl esters, as reported by Bougeard (2009), using a modified version of USEPA Method 552.2 developed by Tung and colleagues (Tung *et al.*, 2006). A flow chart of this process has been summarised in

Appendix 3. The derivatised samples were then stored at -18 °C. Analysis was performed within 14 days of extraction. The vial, containing 2 ml of methyl tert-butyl ether (MTBE) and the HAA methyl esters, was pipetted equally using an automatic pipette into two vials (~ 1 ml) and capped. Each vial was analysed in parallel on a GC-μECD and a Leco Pegasus GC×GC-time of flight mass spectrometer (GC×GC-ToFMS). The instrument parameters used during the experiments are reported in Chapter 3, with the exception that the initial experiments on GC-μECD utilised a SGE BPX5 column.

To help summarise, a flow diagram (describing the stages for sample preparation and subsequent analysis) is provided in Figure 6.1.

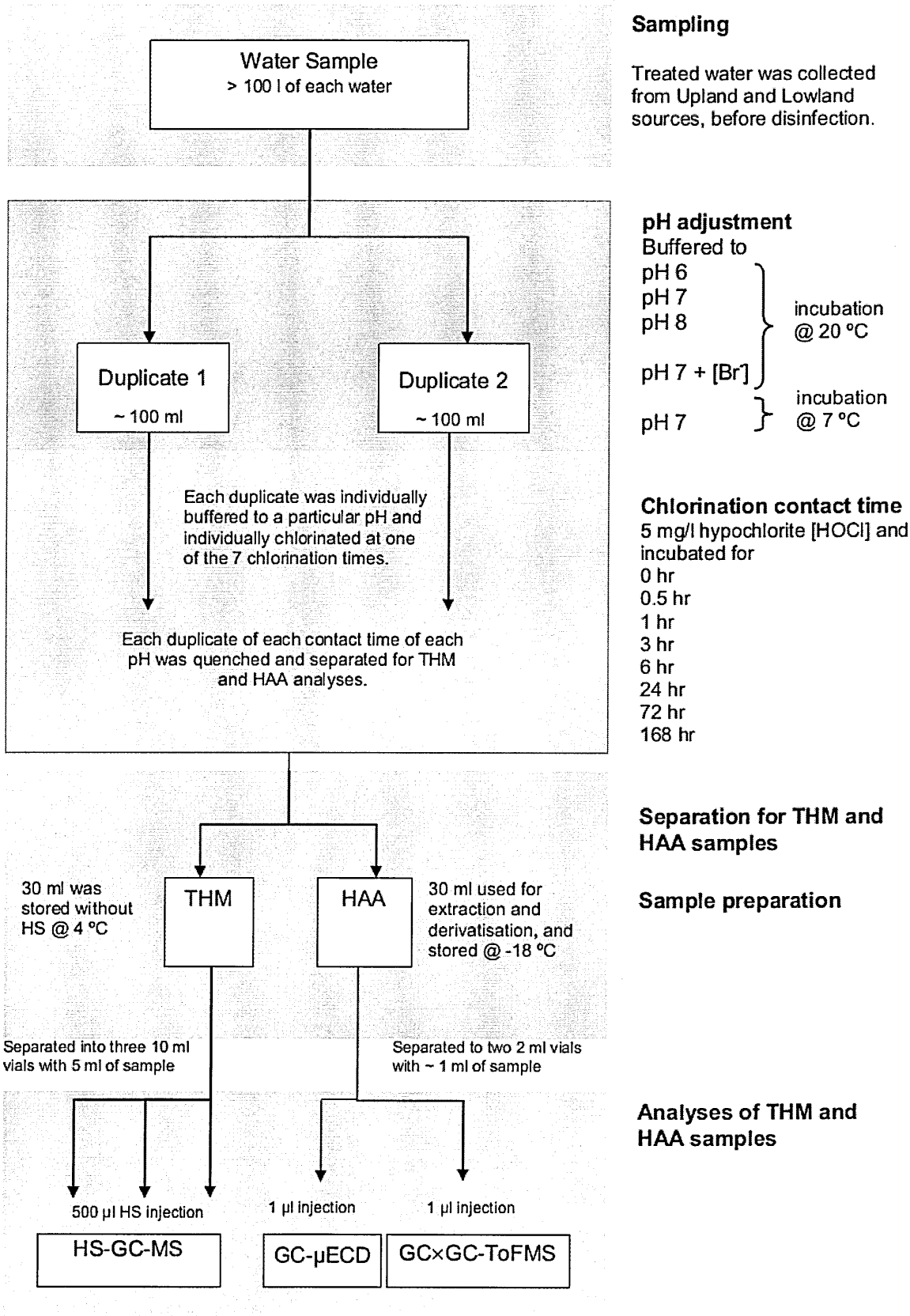


Figure 6.1: A flow diagram of the approach adopted for the evaluation of the formation potential of bulk waters at various contact times, pH and temperature conditions.

6.3 Results for the characterisation of bulk water samples and an evaluation of the validity of HAA concentration measurements

6.3.1 Characterisation of the bulk water samples

Table 6.1 summarises the values obtained for the lowland and upland waters, prior to use.

Table 6.1: Characterisation of the bulk water samples (lowland and upland water)

Parameters	Lowland Water	Upland Water
Bulk Water		
pH	8.0	6.7
$SUVA_{254}$ [1] (l/(mg m))	1.3	2.3
Alkalinity (mg/l of $CaCO_3$)	188	6
Bromide content (µg/l)	206	34
Natural organic matter (mg/l) [2]	4.7	2.1
NOM Fractions [3]	**(%)**	**(%)**
Hydrophilic - acid + neutral (HPI-AN)	40	67
Hydrophobic - acid (HPO-A)	23	19
Transphilic (TPI)	31	8
Hydrophobic - neutral (HPO-N)	2	4
Hydrophilic - base (HPI-B)	4	2

All parameters above were measured by Cranfield University, just prior to analyses.

[1] *$SUVA_{254}$ is the specific ultraviolet absorbance and a useful parameter for the assessment of NOM, calculated as a ratio of the UV absorbance at 254 nm to the dissolved organic carbon content.*
[2] *This is the non-purgeable organic carbon (NPOC) measured using a Shimadzu TOC-5000A analyser.*
[3] *NOM fractions were obtained by Cranfield University using Amberlite™ XAD™ resin adsorption chromatography using a method adapted from Leenheer et al. (2004). This method has been described in Appendix 3.*

It can be seen from Table 6.1, that lowland water had a greater natural organic matter (NOM) concentration (4.7 mg/l) than upland water (2.1 mg/l). NOM fractionation indicated that the organic matter in the upland water had a higher hydrophilic content, whilst the concentrations of hydrophobic matter were similar in both. The lowland water contained a

much greater proportion of transphilic matter. The pH and alkalinity of the two waters were also different. The lowland water was more alkaline with a pH of 8.0 and had a higher concentration of $CaCO_3$ (188 mg/l) whilst the upland water had a pH of 6.7 and an alkalinity of 6 mg/l $CaCO_3$. The bromide content of the lowland water (206 µg/l) was six times higher than the upland water (34 µg/l).

6.3.2 Issues identified with HAA analyses

Chapter 5 discussed the development and optimisation of a number of potential analytical methods that could be utilised for the determination of the concentrations of HAAs. Of these, two were selected for use in this study (GC-µECD (BPX5) and GC×GC-ToFMS). On applying these methods to real water samples, an issue arose when trying to quantify the levels of DCAA with the GC-µECD. In addition, the measurement of MCAA did not provide consistent results, either for duplicates or between instruments. Owing to the short shelf life of the derivatised samples (< 2 weeks), the issues with DCAA were not identified until after all the samples were processed. Further investigations into the sources of the errors were conducted after the study, and the findings are reported below.

DCAA

The DCAA concentrations obtained by GC-µECD were consistently higher than those obtained by the GC×GC-ToFMS on the same sample. Table 6.2 illustrates these findings with a sample of data from the formation potential kinetic experiments, at pH 7, on lowland and upland waters (full data is available in Appendix 5). It can be clearly seen, that in lowland water the DCAA concentration is being overestimated by a factor of approximately 1.49 (1.47 ± 0.15 and 1.52 ± 0.28) and in upland water by a factor of approximately 1.78 (1.70 ± 0.11 and 1.86 ± 0.36).

Table 6.2: The concentrations of DCAA measured in A) lowland water and B) upland water, at pH 7 and various chlorination contact times.

A

Contact time (hours)	DCAA Concentration (µg/l)			
	Sample duplicate 1		Sample duplicate 2	
	GC-µECD	GC×GC-ToFMS	GC-µECD	GC×GC-ToFMS
0.5	5.7	3.6	6.1	5.1
1	4.7	3.5	5.1	4.0
3	6.3	4.3	5.8	2.9
6	6.7	5.6	6.8	5.1
24	14.3	9.5	12.5	8.0
72	21.3	12.8	20.7	13.5
168	32.2	21.4	34.4	19.8

B

Contact time (hours)	DCAA Concentration (µg/l)			
	Sample duplicate 1		Sample duplicate 2	
	GC-µECD	GC×GC-ToFMS	GC-µECD	GC×GC-ToFMS
0.5	11.3	6.9	12.2	7.1
1	12.9	7.2	18.3	7.0
3	18.7	10.0	18.3	10.1
6	20.3	12.3	20.2	10.3
24	30.6	18.0	30.8	19.9
72	43.2	25.1	43.1	25.4
168	51.3	33.9	49.4	30.2

Experiments were then undertaken to identify and establish the source of this discrepancy and which of the two instruments was accurate. The most likely source for the higher concentration reading on the GC-µECD was a co-eluting compound that was ECD active probably a halogenated species. On further examination of the GC×GC-ToFMS total ion chromatograms (Figure 6.2), it became apparent that DCAA was only partially resolved from a co-eluting contaminant, even after separation by a BPX5 and a BPX 50 column.

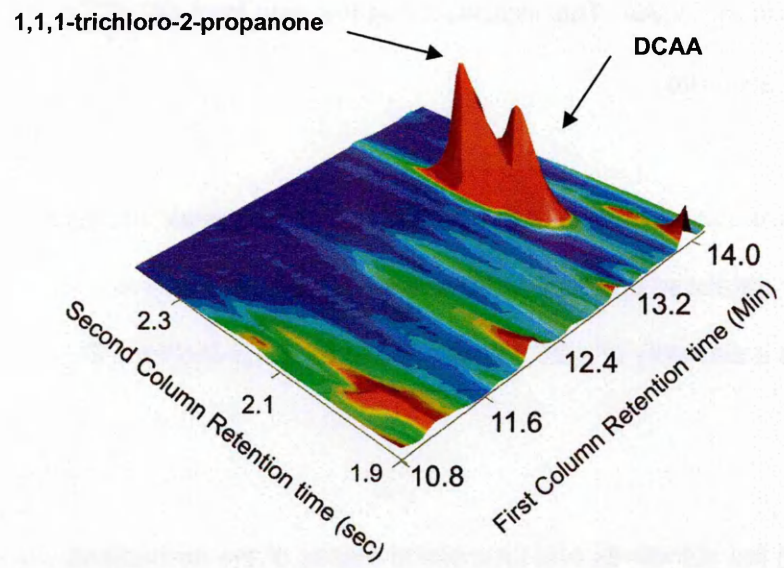


Figure 6.2: A total ion chromatogram of a derivatised upland water sample obtained by GC×GC-ToFMS displayed in 3D relief between the retention times 10.8 - 14.0 min (1st column) and 1.9 - 2.4 sec (2nd column). Columns: SGE BPX5 and SGE BPX50.

As shown in Figure 6.3, the deconvolution algorithm on the Pegasus software resolved the DCAA and co-eluting contaminant by using the *m/z* 59 and *m/z* 43 ions respectively.

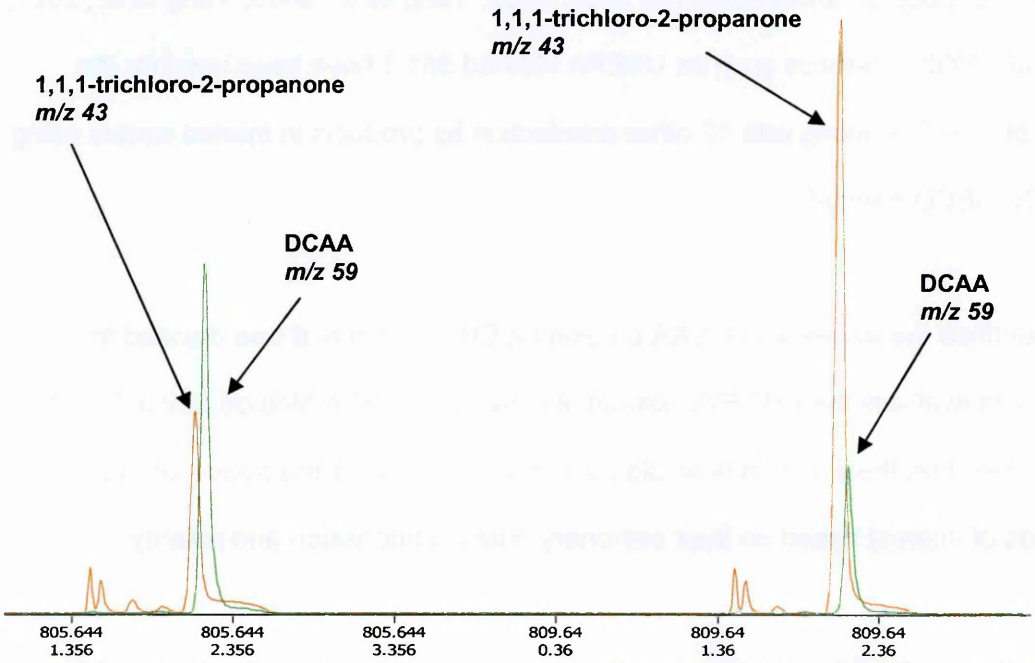


Figure 6.3: 1D GC×GC-ToFMS chromatogram between two modulation periods. The deconvolution algorithm resolved the two compounds using the ion m/z 43 for 1,1,1-trichloro-2-propanone and m/z 59 for DCAA.

The mass fragmentation pattern of the deconvoluted 'DCAA' peak in the TIC was then compared to the NIST library database. A positive identification of the peak with a

similarity of > 95.6% was found for DCAA. This indicated that the data from GC×GC-ToFMS could be reported as accurate.

The deconvoluted mass fragmentation pattern of the partially co-eluting peak was also compared to the NIST library database and a peak table was generated. Positive identification of the peak with a similarity of > 86.5% was found for 1,1,1-trichloro-2-propanone (111-TCP).

111-TCP was not detected in the standards and procedural blanks of the derivatised deionised water that were extracted and analysed in the same way. It was, therefore concluded that it was most likely to have been formed by the chlorination of the contaminants in the bulk water samples.

A survey of literature showed that 111-TCP is a known disinfection by-product that belongs to the group of haloketones (Xu *et al.*, 2002; Yang *et al.*, 2008; Yang *et al.*, 2007; Zhang *et al.*, 2009). Methods such as USEPA Method 551.1 have been used for the detection of 111-TCP along with 12 other disinfection by-products in treated waters using the LLE-GC-μECD method.

Having identified the issues with DCAA on using a BPX5 column, it was decided to purchase and evaluate the DB5.625 column, as used by USEPA Method 552.3. It had been assumed that these columns would have had similar resolving power for the compounds of interest based on their stationary phase composition and polarity.

A comparative study of the columns was then conducted using derivatised HAAs from water samples obtained from lowland and upland treatment plants. As can be seen from Table 6.3, the DCAA results from the GC×GC-ToFMS and the GC-μECD (J&W DB 5.625) gave comparable results for both the waters, while the GC-μECD (SGE BPX5) resulted in significantly higher levels of DCAA, as previously found. The DB 5.625 column resolved

the co-eluting compound from DCAA, as shown in Figure 6.4. In addition, there was a slight increase in retention time for DCAA on the DB 5.625 column, which was likely to be because of the different partitioning of the compound on the stationary phases, further indicating they were not completely identical. These findings confirm the advice in the USEPA methods always to confirm the suitability of the column chosen for the particular analyte and water samples being studied. These findings would also suggest there may be issues with the values reported in the literature as summarised in Table 5.1 in Chapter 5. Further investigations of the specific stationary phases would need to be conducted.

Table 6.3: The concentrations of DCAA as obtained by GC-μECD (SGE BPX 5), GC-μECD (J&W 5.625) and GC×GC-ToFMS (SGE BPX5 and SGE BPX50).

	Upland Water	Lowland Water
GC-μECD (BPX 5)	1061.11 ± 55.5	1530.61 ± 65.5
GC-μECD (J&W DB 5.625)	215.55 ± 13.50	200.11 ± 14.53
GC×GC-ToFMS (SGE BPX5 and SGE BPX50	216.9 ± 10.50	210.44 ± 15.50

Duplicate analyses performed for each method.

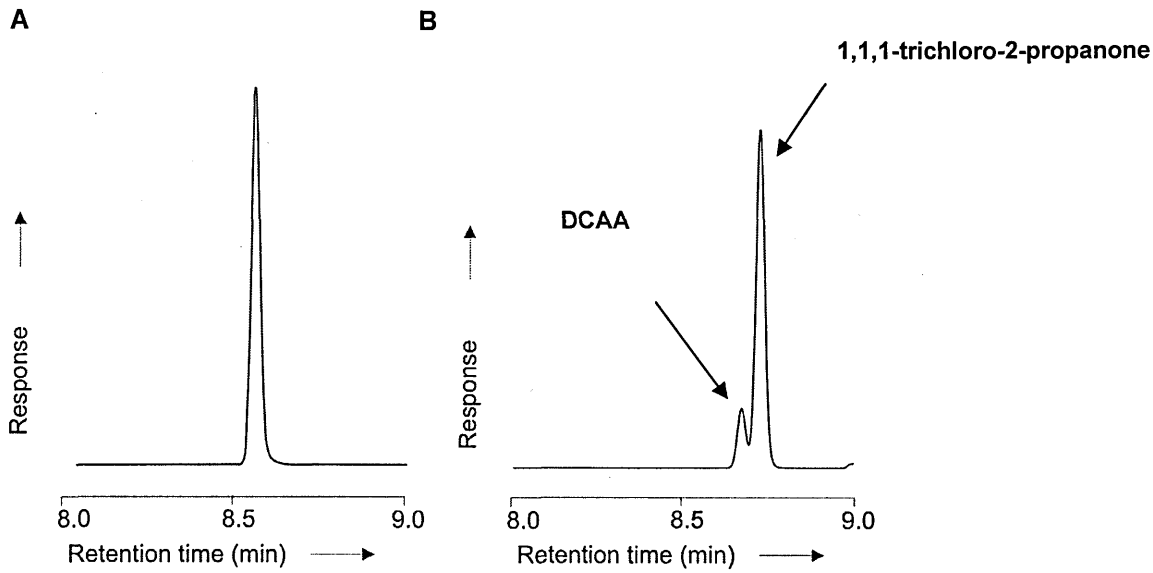


Figure 6.4: Chromatograms of the GC-μECD with A) the SGE BPX5 column and B) the J&W DB 5.625 column, at retention times between 8.0 - 9.0 min. The co-eluting compound was sufficiently resolved from the DCAA on the J&W DB 5.625 column to allow quantitation.

Given the complexity of the sample preparation and derivatisation, and the number of samples analysed during this study, the study was not repeated with the DB5.625 column and GC-μECD. Whilst the formation potential study was conducted with both GC-μECD (BPX5) and GC×GC-ToFMS, the poor agreement between GC-μECD (BPX5) with the other two, coupled with the good agreement between GC-μECD (DB 5.625) and GC×GC-ToFMS, for DCAA, meant that only the data for GC×GC-ToFMS are reported in subsequent sections.

MCAA

The concentration obtained for MCAA, for both the duplicates and the two instruments (GC×GC-ToFMS and a GC-μECD), were inconsistent. For example, the MCAA concentration measured by the GC-μECD, in duplicate samples of lowland water, at pH 7, after 168 hours of chlorination was 8.9 μg/l and 15.8 μg/l. The concentrations measured by the GC×GC-ToFMS for the same duplicate samples were 4.4 μg/l and 3.3 μg/l respectively (Table 6.4 A).

In another example, it can be seen that MCAA concentrations obtained by the GC-μECD for an upland water sample, after 3 hours contact time, was 60.3 μg/l and 14.1 μg/l. However, the GC×GC-ToFMS measured the same duplicate samples with a concentration of 30.4 μg/l and 4.7 μg/l respectively (Table 6.4 B).

Table 6.4 displays only a sample of the MCAA data, however, this inconsistency was observed throughout the formation potential experiments in both lowland and upland waters. The full MCAA concentration data is available in Appendix 5.

Table 6.4: The concentrations of MCAA present in A) lowland water and B) upland water, at pH 7, at various chlorination contact times.

A

Contact time (hours)	MCAA Concentration (µg/l)			
	Sample duplicate 1		Sample duplicate 2	
	GC-µECD	GC×GC-ToFMS	GC-µECD	GC×GC-ToFMS
0.5	0.8	n/d	0.5	n/d
1	3.0	n/d	2.8	n/d
3	3.1	n/d	1.3	n/d
6	4.1	n/d	5.9	0.4
24	14.7	3.2	5.1	1.4
72	10.3	3.1	8.5	3.2
168	8.9	4.4	15.8	3.3

B

Contact time (hours)	MCAA Concentration (µg/l)			
	Sample duplicate 1		Sample duplicate 2	
	GC-µECD	GC×GC-ToFMS	GC-µECD	GC×GC-ToFMS
0.5	14.4	10.1	24.4	9.5
1	15.3	3.3	17.6	2.2
3	60.3	30.4	14.1	4.7
6	19.6	7.9	17.2	5.7
24	20.8	7.3	79.0	68.2
72	33.9	7.0	34.2	9.6
168	27.9	7.5	30.1	4.2

n/d – not detected above the instrument detection limits.

A review of the literature indicated that similar problems in measuring MCAA concentrations using a GC-µECD had been reported (Malliarou *et al.*, 2005; Reckhow *et al.*, 2008). No reasons were given: however, one possible explanation is that MCAA (and its volatile methyl ester) were lost during either extraction, preparation, derivatisation prior to analysis of the sample. This is analogous to the finding previously reported for THMs in Chapter 4. As a consequence of the highly variable results obtained, concentration values for MCAA were not reported in this study.

6.3.3 Evaluation of the reproducibility of HAA concentrations on both instruments

The concentrations of the remaining HAA6 species: MBAA, TCAA, BCAA and DBAA, in treated water samples, obtained by GC×GC-ToFMS and GC-μECD, were compared to evaluate their reproducibility and therefore the analytical accuracy. The results obtained for both water types at pH 7, after 168 hours of contact, are provided in Table 6.5. The full data set for all the samples can be found in Appendix 5.

Table 6.5: The concentrations of MBAA TCAA, BCAA and DBAA obtained by GC-μECD and GC×GC-ToFMS for A) upland water and B) lowland water, at pH 7, after 168 hours of contact.

A

	GC-μECD		GC×GC-ToFMS	
MBAA	2.10	± 0.02	2.00	± 0.12
TCAA	8.15	± 0.08	8.10	± 0.68
BCAA	25.76	± 0.27	23.93	± 1.24
DBAA	13.74	± 0.34	15.92	± 0.75

B

	GC-μECD		GC×GC-ToFMS	
MBAA	n/d		n/d	
TCAA	48.97	± 0.18	48.70	± 2.03
BCAA	4.40	± 0.07	4.06	± 0.20
DBAA	n/d		n/d	

Duplicate analyses performed on each instrument. n/d - not detected

In lowland water, the results for MBAA, TCAA, BCAA and DBAA were in good agreement between the two instruments. In upland water, the TCAA and BCAA concentrations were also in good agreement, while the remaining HAAs (MBAA and DBAA) were below the detection limits. It can, therefore, be concluded that concentrations for the four HAAs (MBAA, TCAA, BCAA and DBAA), determined by the two instruments, were within acceptable deviations of < 25 % (USEPA, 2003).

Summary of the finding in Sections 6.3.2 and 6.3.3

In the US, the five regulated HAAs are MCAA, MBAA, DCAA, TCAA and DBAA, the total HAA concentration is therefore reported as HAA5. Given that MCAA could not be measured accurately in this study, the approach of Bougeard *et al.* (2008) was applied, and therefore within this study we report the total concentration for HAAs as HAA5*. The main difference being that MCAA is replaced with BCAA.

However, because of the issues reported in Section 6.3.2 for the measurement of DCAA using the BPX5 column with a GC-μECD, the results reported for HAA concentrations in the Sections 6.3. were obtained on the GC×GC-ToFMS.

6.4 Results and discussion for the formation of THMs and HAAs in treated UK waters

As reported in other similar studies (Hwang *et al.*, 2002; Liang *et al.*, 2003; Singer *et al.*, 1999), the concentrations of THMs and HAAs were plotted against the contact times to evaluate the influences of the different parameters. Throughout, lines connecting the different data points within a series have been added to make any trends clearer to visualise. Tables detailing the results obtained in the following sections are available in Appendix 5. In contrast to previous chapters, a formal discussion of the results for THMs and HAAs will be provided following each of the sections.

6.4.1 Results for the investigation of the influence of pH and contact time on the formation of THMs and HAAs during chlorination

6.4.1.1 THM4

As expected, the total THM concentration (THM4) increased with the chlorination contact time, as shown by Figure 6.5 (lowland water) and Figure 6.6 (upland water). The THM4 concentrations followed the general trend of rapid formation with a steep slope (6 hours),

followed by with a more gradual increase up to the full 7 days of contact time. The same trend was found for all the three pH levels (6, 7 and 8).

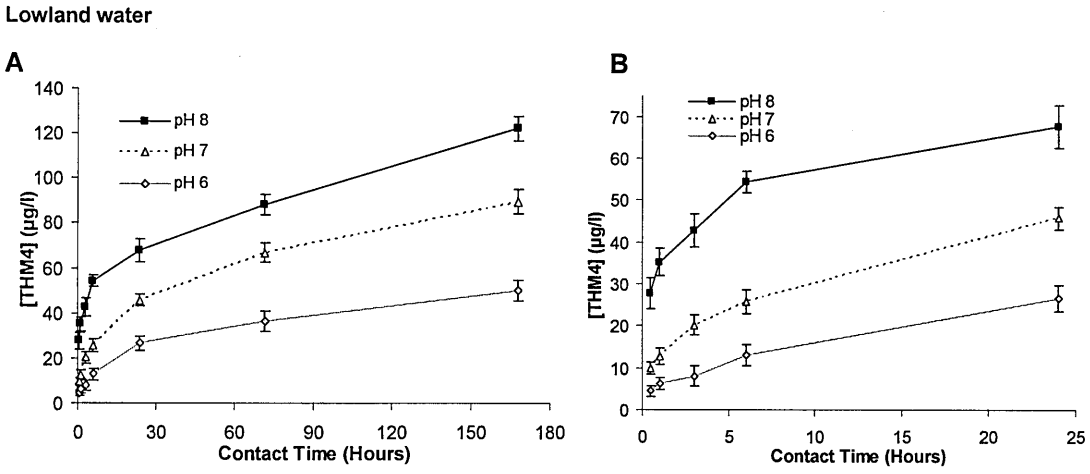


Figure 6.5: [THM4] at the various contact times, at pH 6, 7 and 8 for the lowland water source, A) over 168 hours and B) expanded between 0.5 - 24 hours. Error bars are the cumulative error of the sum of the mean concentrations, n=6.

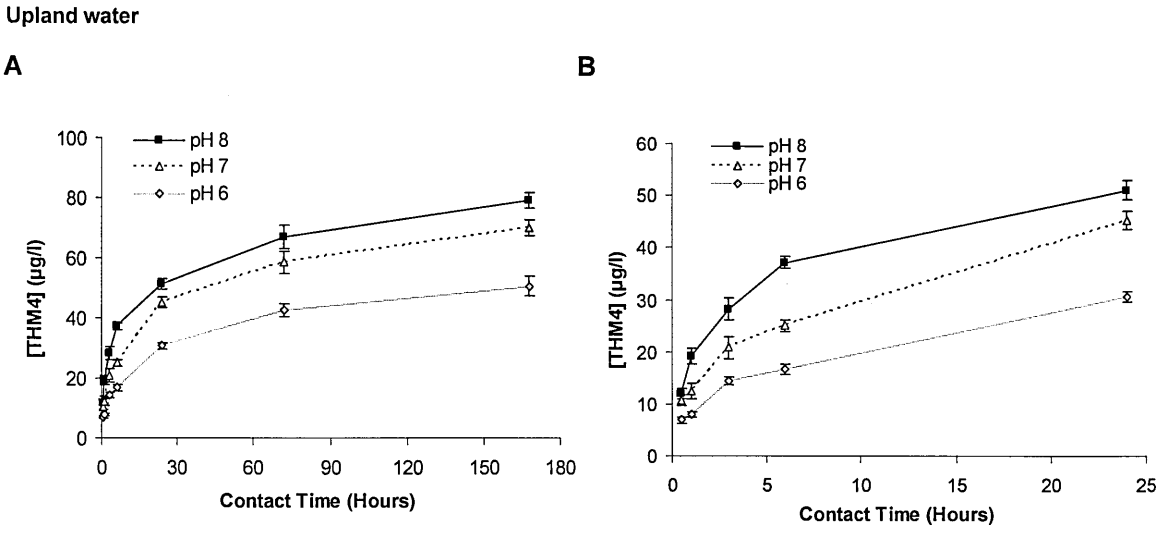


Figure 6.6: [THM4] at the various contact times, at pH 6, 7 and 8 for the upland water source, A) over 168 hours and B) expanded between 0.5 - 24 hours. Error bars are the cumulative error of the sum of the mean concentrations, n=6.

In the lowland water, after 168 hours of contact time, at a pH of 7, the THM4 concentration was 1.8 times higher than at pH 6. pH 8 resulted in a 2.4 times increase in THM4 concentration over that obtained at pH 6. Similarly, in upland water the THM4

concentration increased by 1.4 and 1.6 times, respectively. The expanded graphs of the THM4 concentrations below < 25 hours show this trend in more detail. The cumulative error bars are the sum of the mean for each THM, derived from triplicate analyses of duplicate samples of each THM (n=6).

For a more detailed understanding of the process occurring, the influence on the concentrations of the individual THMs were examined.

6.4.1.2 Individual THMs in lowland water

The most abundant THMs formed during chlorination of lowland water were $CHCl_2Br$ and $CHClBr_2$, followed by $CHCl_3$ and $CHBr_3$. Given the elevated levels of bromide (206 µg/l), as reported in Section 6.3.1, these results are not unexpected. The influence of increased bromide concentrations on the profile of individual THMs will be investigated further in Section 6.4.3. At all three pH conditions, the individual THM concentrations showed a rapid increase followed by a more gradual rise, as shown in Figure 6.7.

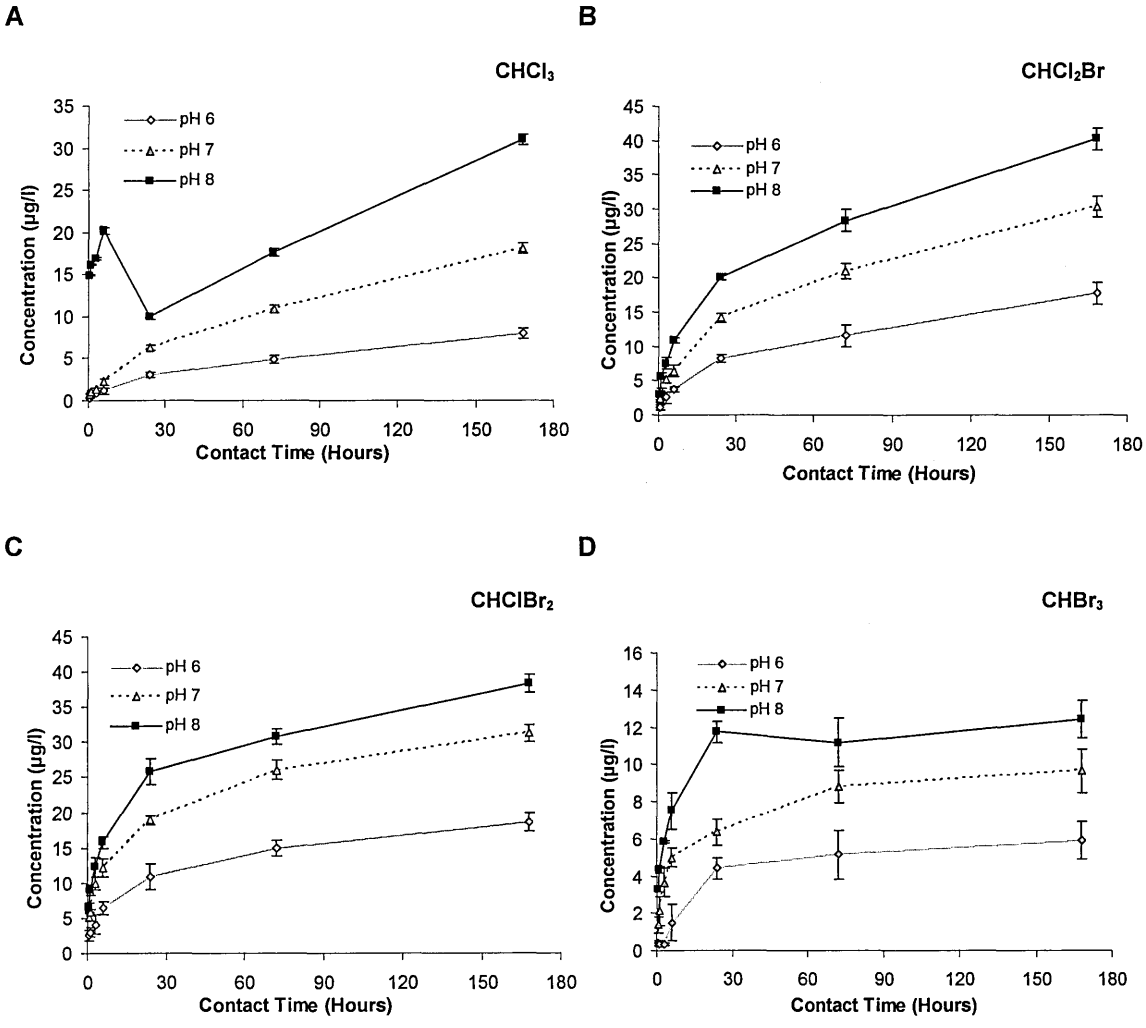


Figure 6.7: The influence of pH on the concentrations of individual THM species for a lowland water throughout the full chlorination contact period; A) $CHCl_3$, B) $CHCl_2Br$, C) $CHClBr_2$ and D) $CHBr_3$. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

All four THMs followed the same general trend; however, there was an anomaly in the $CHCl_3$ formation pattern at contact times less than 25 hours and at pH 8. The $CHCl_3$ concentration at the contact time of 0.5 hours was unusually high (14.9 µg/l). After 6 hours of contact, this concentration increases to 20.2 µg/l, followed by a sharp decrease to 10.0 µg/l after 24 hours. This is then followed by an increase to 17.6 and 31.2 µg/l at the 72 and 168 hour contact time respectively. The cause of this trend was unknown; however, one possible explanation could be that since the samples are independently prepared, a $CHCl_3$ contamination was introduced during the sample preparation stages. The excellent reproducibility of the duplicate samples suggests that the anomaly is representative of the sample and not an artefact of instrument analysis. These experiments could not be

repeated; however, our colleagues were informed of the issue and an even greater consideration will be given to sample preparation in the future.

The influence of pH on the formation rates of each of the individual THMs is also illustrated by Figure 6.7. The highest concentration for each THM was found at pH 8, whereas the lowest concentration was found at pH 6. $CHClBr_2$ was the most abundant; however, $CHCl_3$ was most influenced by a change in the pH of the water. After 168 hours of contact, an increase in the pH from 6 to 7 resulted in an increase in $CHCl_3$ concentration by 2.2 times. Similarly in going from pH 6 to 8, the $CHCl_3$ concentration increased by 3.9 times.

6.4.1.3 Individual THMs in upland water

After seven days (168 hours), the most abundant THM formed during chlorination of upland water was $CHCl_3$ (82.9 %) followed by $CHCl_2Br$ (17.1 %). Upland water did not contain $CHClBr_2$ and $CHBr_3$. This composition was most probably because of the much lower levels of bromide (34 µg/l) present, as reported in Section 6.3. At all three pH conditions, the individual THM concentrations showed a rapid increase followed by a more gradually rise, as illustrated in Figure 6.8.

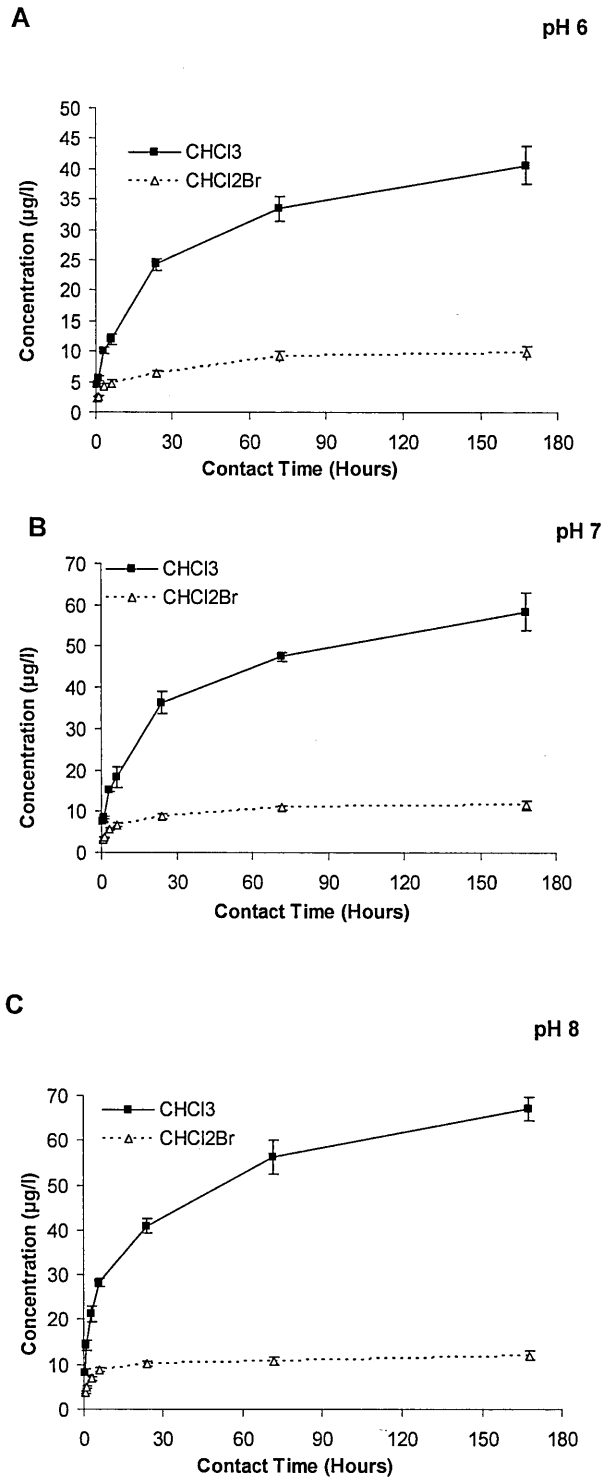


Figure 6.8: The concentrations of the individual THM species in upland water over the full chlorination contact period; A) pH 6 B) pH 7 and C) pH 8. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

The influence of pH on individual THMs in upland water is illustrated by Figure 6.9. In agreement with the lowland water findings, $CHCl_3$ concentrations were highest at pH 8, than pH 7 and pH 6. However, after 168 hours of contact, an increase in pH from 6 to 7 and than to pH 8, resulted in smaller increases in $CHCl_3$ concentrations (1.4 and 1.6 times respectively) in contrast to lowland samples. No such correlation could be drawn for $CHCl_2Br$.

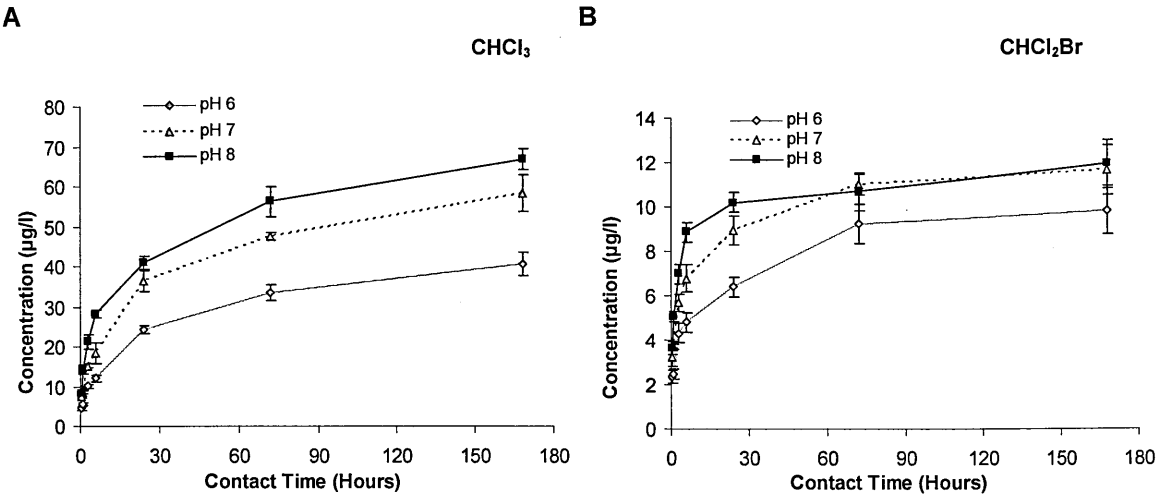


Figure 6.9: The influence of pH for the upland water over the full chlorination contact period on the concentrations for A) $CHCl_3$, and B) $CHCl_2Br$. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

6.4.1.4 HAA5*

As may have been anticipated from the profiles generated for the individual THMs, both lowland and upland water showed a sharp rise in HAA5* concentration in the first 6 hours, followed by a more gradual rise, as illustrated by Figures 6.10. In lowland water, adjustment of the pH did not significantly influence the concentrations of HAA5*. However, in upland water, the pH had a greater influence on the HAA5* concentrations. The concentrations of HAA5* at pH 8 were higher than pH 6 and pH 7 for the whole chlorination period. At the 168 hour contact time, the concentration of HAA5* was 1.5 times higher at pH 8 than at pH 6 and 7. The error bars are cumulative error for the sum of the mean HAA values from duplicate analysis.

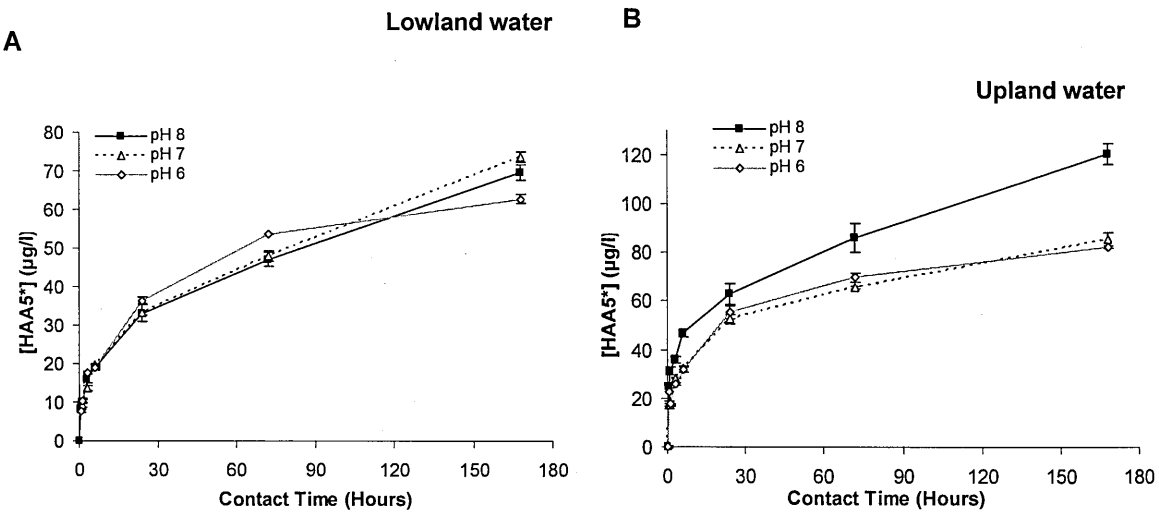


Figure 6.10: [HAA5] at the various contact times at pH 6, 7 and 8, for A) lowland water B) upland water. Error bars are the cumulative error of the sum of the mean concentrations.*

6.4.1.5 Individual HAAs in lowland water

All five HAAs were observed above their detection limits. Generally, BCAA was the most abundant HAA in this water, while MBAA was the least abundant. The change in concentration of each HAAs, at each pH, over the contact period, can be seen in Figure 6.11. At all three pH conditions, the individual HAA concentrations showed a rapid increase followed by a more gradually rise.

After 168 hours of contact, the DCAA concentration was 1.4 times higher at pH 8 and pH 7 than at pH 6. In contrast, the BCAA followed the trend pH 7 > pH 6 > pH 8. However, prior to 120 hours of contact, the BCAA levels were highest at pH 6 followed by pH 7 and pH 8. Similarly, after 168 hours, DBAA levels were 1.4 times higher at pH 7 and pH 8, relative to pH 6. At 90 hours of contact, DBAA concentrations were higher at pH 8 than at pH 7 and pH 6. No such correlations could be drawn for TCAA and MBAA as their concentrations are comparatively much lower (<10 µg/l), and as such the data points overlap.

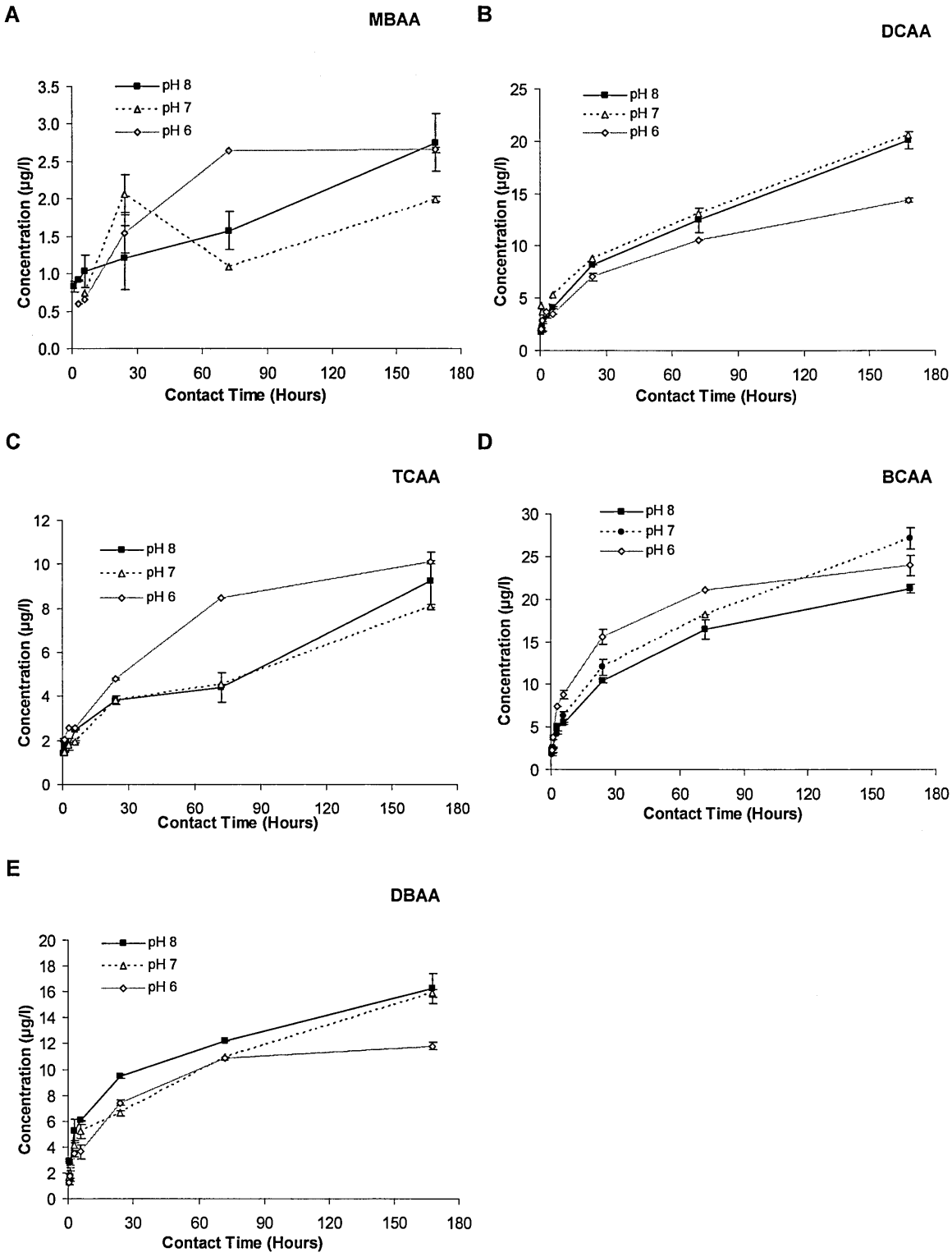


Figure 6.11: The influence of pH on the concentrations of individual HAA species for lowland water over the full chlorination contact period; A) MBAA, B) DCAA, C) TCAA, D) BCAA and E) DBAA. Error bars are the spread of the duplicate concentration measurement.

6.4.1.6 Individual HAAs in upland water

As anticipated from the bromide levels present in the bulk water samples and consistent with the findings of the THMs, only three HAAs were observed above the detection limits (DCAA, TCAA and BCAA). TCAA was the most abundant HAA species, whilst BCAA was least abundant species detected, as illustrated in Figure 6.12.

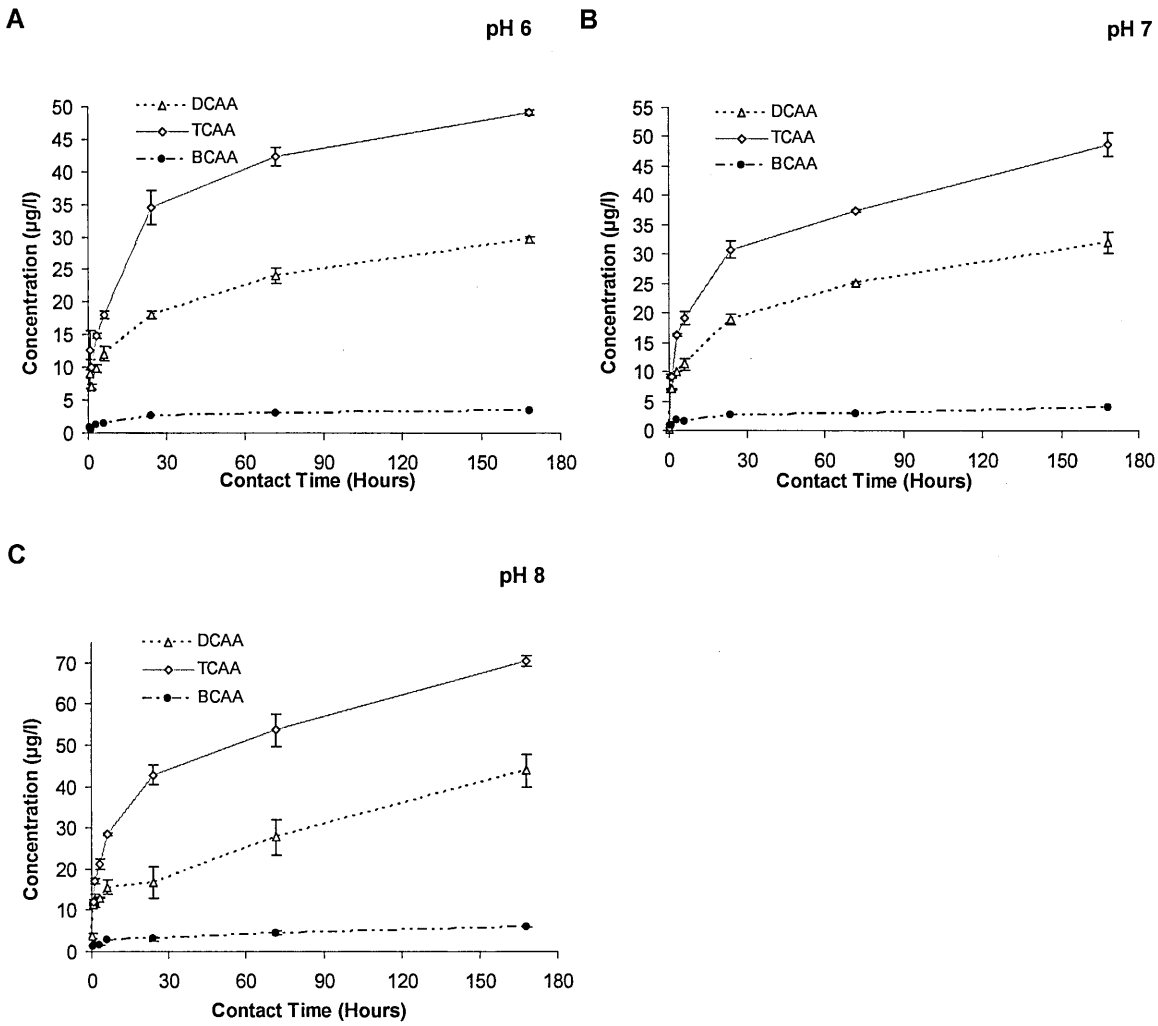


Figure 6.12: The concentrations of the individual HAA species present in upland water over the full chlorination contact times period; A) pH 6, B) pH 7 and C) pH 8. Error bars are the spread of the duplicate concentration measurement.

The influence of pH on the formation of each of the three HAAs in upland water, is illustrated in Figure 6.13. After 168 hours, DCAA concentration was on average 1.6 times higher at pH 8 relative to pH 6 and pH 7. TCAA concentrations were consistently higher at

pH 8 compared to pH 6 and pH 7. BCAA levels at pH 8 were also found to be higher when compared to pH 6 and pH 7, even though their concentrations were below 6 µg/l.

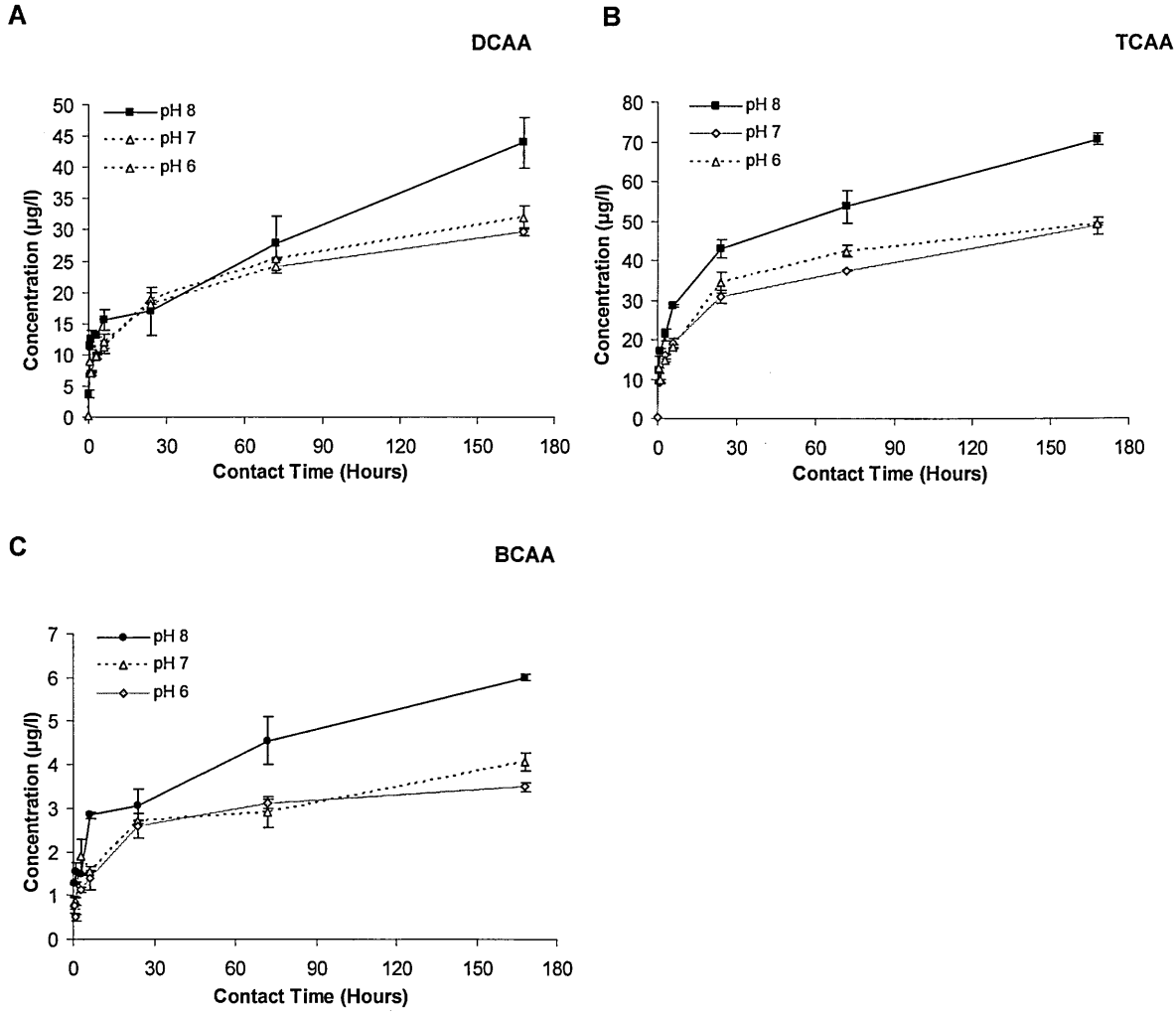


Figure 6.13: The influence of pH on the concentrations of the individual HAA species in the upland water over the full chlorination contact period; A) DCAA, B) TCAA and, C) BCAA. Error bars are the spread of the duplicate concentration measurement.

6.4.2 A discussion of the influence of pH and contact time on the formation of THMs and HAAs during chlorination

As reported in Chapter 1, chlorination contact (or residence) time for the reaction of the chlorine with the NOM is an important factor in the formation of DBPs, because of the presence of residual chlorine to prevent the re-growth of harmful microorganisms in drinking water distribution systems. This study has shown that the longer the chlorination contact time, the more THMs and HAAs are formed, replicating the findings reported in the literature. Researchers have demonstrated that the concentrations of DBPs typically

increase with contact time, until the reaction is chlorine limited (Carlson *et al.*, 1998; El-Dib *et al.*, 1995; El-Shafy *et al.*, 2000; Fleischacker *et al.*, 1983; Krasner *et al.*, 1996; Nikolaou *et al.*, 2004a; Westerhoff, 2006). Water treatment plants commonly have a 30 - 120 minutes contact time, prior to entering the distribution system, where it could stay in contact for several hours to days, typically around 1 - 3 days, but anything up to 7 days (Westerhoff, 2006).

The influence of pH on THMs

This study has shown similar trends to those previously reported in the literature, with an increase in both individual THM and THM4 concentrations, with increases in pH from 6 to 8, in both lowland and upland waters. Liang and Singer showed that increasing pH from 6 to 8 increased THM4 concentrations (Liang *et al.*, 2003). Others have reported similar findings (El-Dib *et al.*, 1995; Garcia-Villanova *et al.*, 1997; Nikolaou *et al.*, 2004a; Parsons *et al.*, 2006a; Xie, 2003). Singer and Recknow (2010) reported that although pH can influence chlorination reactions in many ways, it was probably hydrolysis of NOMs that has the greatest effect on THM formation (Singer *et al.*, 2010a). Similar findings were previously reported by Trussell and Umphres (1978), who suggested that THM formation consisted of alternate hydrolysis and halogenation steps (Trussell *et al.*, 1978). Other researchers also reported that higher pHs led to increased THM formation because of hydrolysis (Carlson *et al.*, 1998; Chawla *et al.*, 1983). The relative difference in THM4 concentrations between the two waters could be explained by the dissimilar NOM concentrations, NOM composition and bromide levels. As reported earlier, lowland water had a greater NOM concentration (4.7 mg/l) than upland water (2.1 mg/l). The direct influence of bromide ion concentrations will be investigated later in Section 6.4.3.

Under the formation potential conditions used in this study, it was noted that the lowland water would fail UK THM regulations at pH 8, if measured after 168 hours, but upland water would remain below the regulated limit at all three pH conditions. However, it should be noted that this experiment were conducted 20 °C.

The influence of pH on HAAs

In contrast to THMs, there is less agreement in the literature on the influence of pH on HAA concentrations. In this study, the HAA5* concentrations (MCAA excluded) in lowland water did not appear to have a strong dependence on pH. DCAA concentrations did not show much response to changes in pH between 7 and 8, but the response was lower at pH 6. However, in upland water, HAA5* concentrations increased with a rise in pH from 6 and 7 to pH 8. DCAA, TCAA and BCAA concentrations at pH 8 were higher than at pH 7 and 6. Liang and Singer reported that HAA9 concentrations tended to be greater at pH 8 than pH 6; however, TCAA and DBCAA concentrations decreased with an increase in pH, while MCAA, MBAA, BCAA, DCAA and DBAA did not show any significant influence on changing the pH (Liang *et al.*, 2003). Carlson and Hardy reported that total HAA6 formation increased with a decrease in pH; however, this was dependent on individual concentrations of the HAAs present (Carlson *et al.*, 1998). However, Singer and Recknow (2010) also suggested that other DBPs, such as the HAAs, are unaffected by hydrolysis but their formation pathways may be altered at high pH, resulting in lesser formation. They noted that the dihaloacetic acids have a different formation pathway and pH dependency than the trihaloacetic acids. Dihaloacetic acids are relatively independent of pH whereas trihaloacetic acid formation decreases with increasing pH (Singer *et al.*, 2010b). These findings for TCAA and DCAA have not been entirely replicated in this study. These differences could be attributed to the differing hydrophobic and hydrophilic compositions of NOM in the water two samples, further illustrating the need to conduct the studies on representative samples in the UK. It could also be explained by the dissimilar NOM concentrations (lowland water (4.7 mg/l) and upland water (2.1 mg/l)) and bromide levels.

6.4.3 The results on the influence of bromide ions on the formation of THMs and HAAs

The influence of bromide content on the formation of THMs and HAAs during chlorination, on both lowland and upland water, was investigated. As previously reported, the natural

bromide content in the lowland water (206 µg/l) was six times higher than the upland water (34 µg/l). Both the upland and lowland water samples were spiked with 200 µg/l of bromide and buffered to pH 7. The spiked results were then compared to those obtained for natural bromide content (un-spiked) at pH 7.

6.4.3.1 THM4

As illustrated by Figure 6.14, the THM4 concentrations were consistently higher in the spiked waters, at all contact times, in both lowland and upland waters. In lowland water, after 168 hour exposure, the THM4 concentration increased from 70.1 µg/l, under natural bromide concentrations (206 µg/l), to 110.7 µg/l when spiked. Similarly, in upland water the THM4 concentration, after 168 hours of exposure, was found to increase from 89.4 µg/l to 143.3 µg/l on spiking.

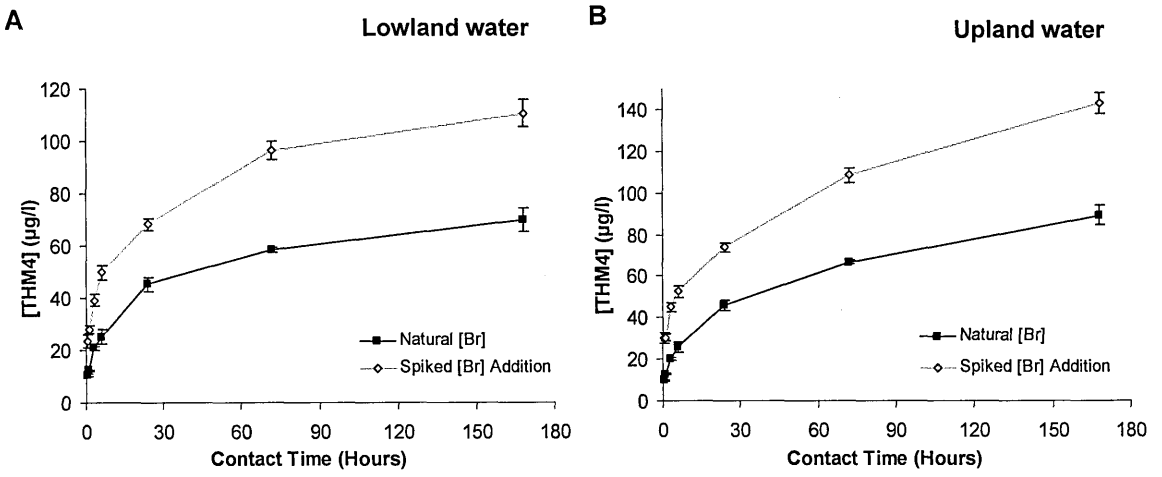


Figure 6.14: The concentrations of the THM4, at pH 7, at the various chlorination times under natural and spiked conditions, in A) lowland water B) upland water. Error bars are the cumulative error of the sum of the mean concentrations, n=6.

6.4.3.2 Individual THMs in lowland water

All four THMs were present in lowland water at natural bromide levels. As illustrated by Figure 6.15, the concentrations of all four of the THMs was higher on spiking, with what was effectively a doubling of the bromide concentration. After 168 hours of contact, $CHBr_3$ increased by 2.7 times, whilst the $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ concentrations had increased by 1.6, 1.2 and 1.7 times, respectively.

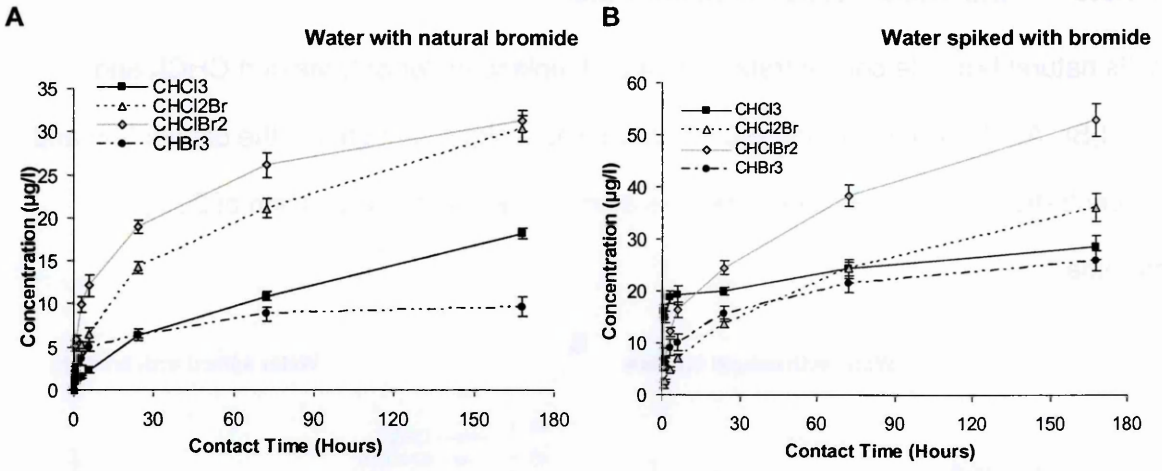


Figure 6.15: The concentrations of the individual THM species at the various chlorination contact times for the lowland water under A) natural and B) spiked conditions. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

The relative distribution of the THMs, after 168 hours of chlorine contact, has been illustrated in Figure 6.16. On spiking, the proportion of $CHCl_3$ remained constant at 20 %, the $CHClBr_2$ and $CHBr_3$ proportions increased from 35 % and 11 % to 37 % and 18 %, respectively. While $CHCl_2Br$ decreased to 25% from 34 %.

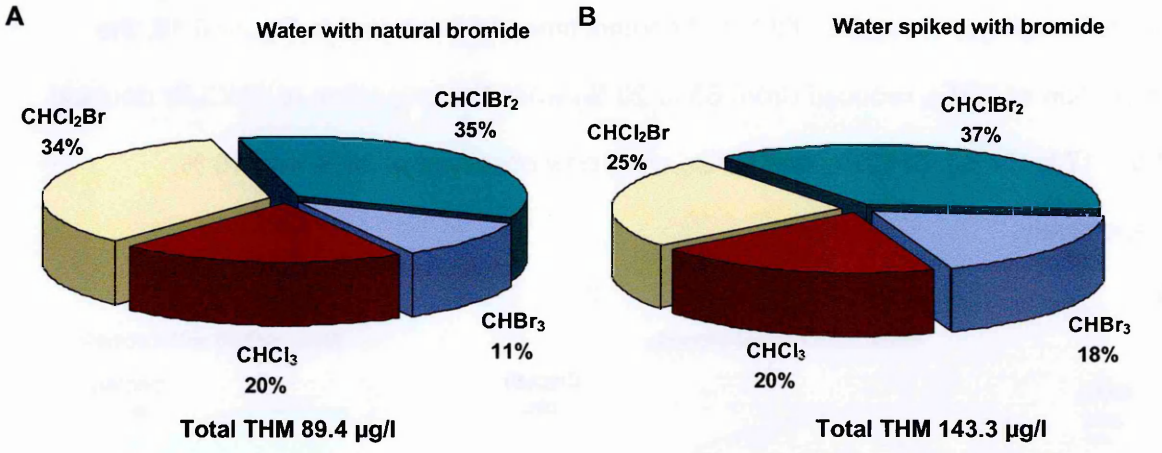


Figure 6.16: Pie charts showing the distribution of THMs after 168 hours of contact time, in lowland water, under A) natural and B) spiked conditions.

6.4.3.3 Individual THMs in upland water

At its natural bromide concentration of 34 µg/l, upland water only yielded $CHCl_3$ and $CHCl_2Br$. As illustrated by Figure 6.17, there was a significant shift in the distribution and concentrations of the THMs favoured, as a consequence of the addition of 200 µg/l of bromide.

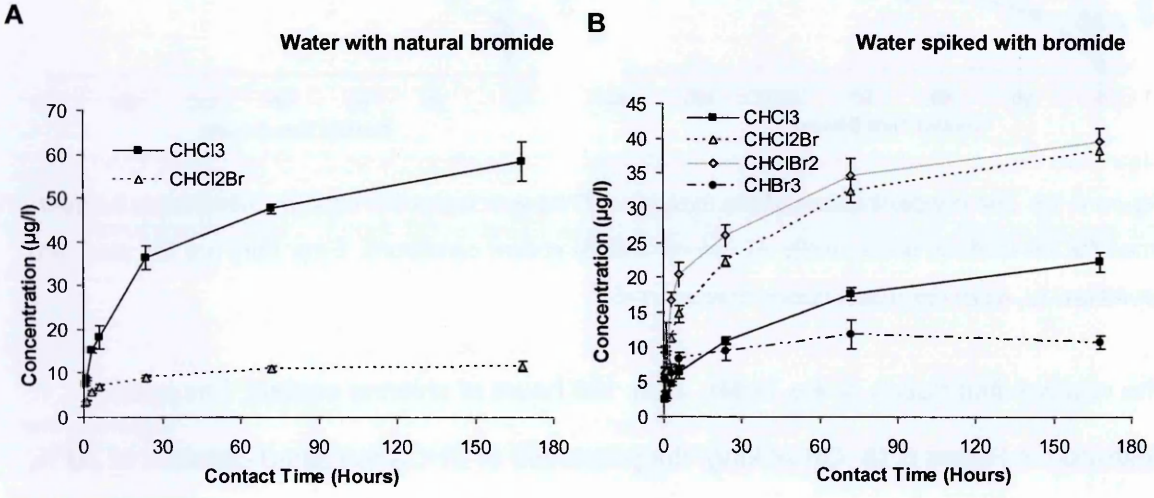


Figure 6.17: The concentrations of the individual THM species at the various chlorination contact times, in upland water, under A) natural and B) spiked conditions. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

The concentration of $CHCl_3$ is significantly lower while the concentrations of the other THMs is higher, across the 168 hrs of contact time. As illustrated in Figure 6.18, the proportion of $CHCl_3$ reduced (from 83 to 20 %) while the proportion of $CHCl_2Br$ doubled (from 17 to 34 %). $CHClBr_2$ and $CHBr_3$ were now observed at 36 % and 10 %, respectively.

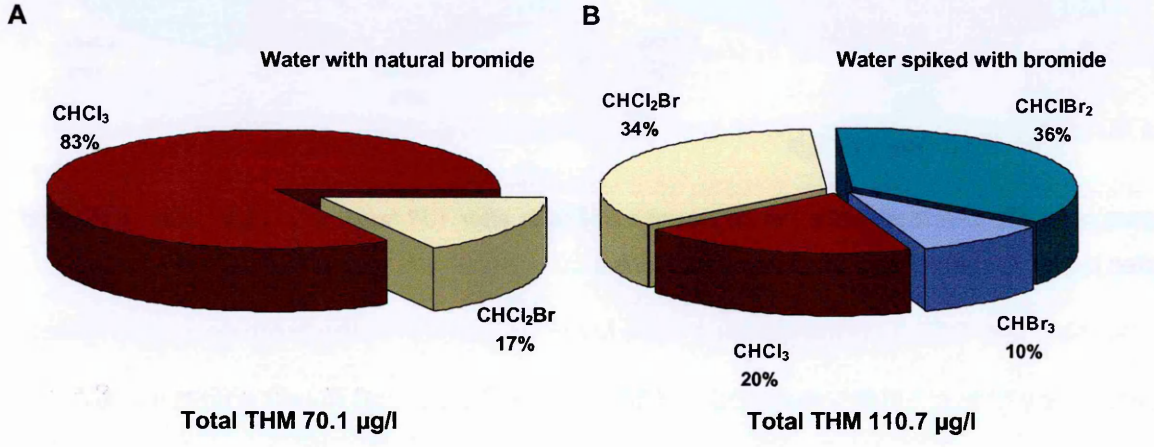


Figure 6.18: A pie chart showing the distribution of THMs at the 168 hour contact time, in upland water, under A) natural and B) spiked conditions.

6.4.3.4 HAA5*

As shown by Figure 6.19, the spiking with bromide resulted in only a small change in the HAA5* concentrations, for the lowland water. After 168 hours, the total HAA5* concentration in the un-spiked water was 73.7 µg/l. In the spiked water, the total concentration of HAA5* was 75.6 µg/l.

In upland water, the HAA5* concentration was significantly lower in the spiked waters After 168 hours, the total HAA5* with natural bromide levels was 85.5 µg/l. However, in the spiked water, the total HAA5* was 0.7 times lower at 55.4 µg/l. This pattern was repeated at all contact times.

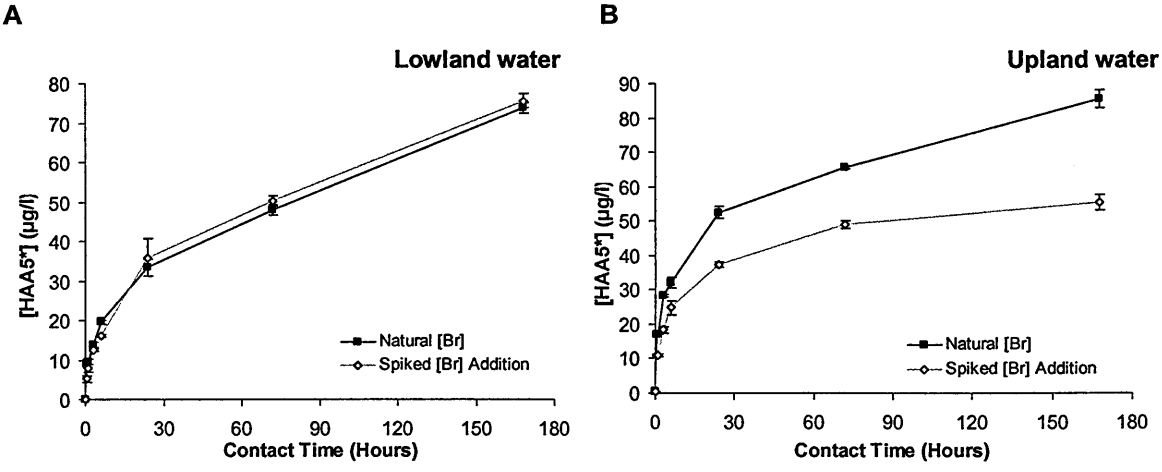


Figure 6.19: [HAA5] at full contact times, at pH 7, under natural and spiked conditions for A) lowland and B) upland waters. Error bars are the cumulative error of the sum of the mean concentrations.*

6.4.3.5 Individual HAAs in lowland water

As illustrated in Figure 6.20, BCAA was the most prominent HAA present in both natural and spiked waters. BCAA levels were slightly elevated in the spiked water sample (1.1 times). As may have been anticipated, DBAA concentrations were higher (1.5 times); conversely, the DCAA concentrations were lower (0.6 times) in the bromide-spiked water across the whole chlorination period. DBAA became the second most important HAA, replacing DCAA in the spiked water. MBAA concentrations were slightly higher while

TCAA were lower; however, their concentrations were still relatively low (< 6 µg/l) in both waters precluding any meaningful information on the correlation with bromide levels.

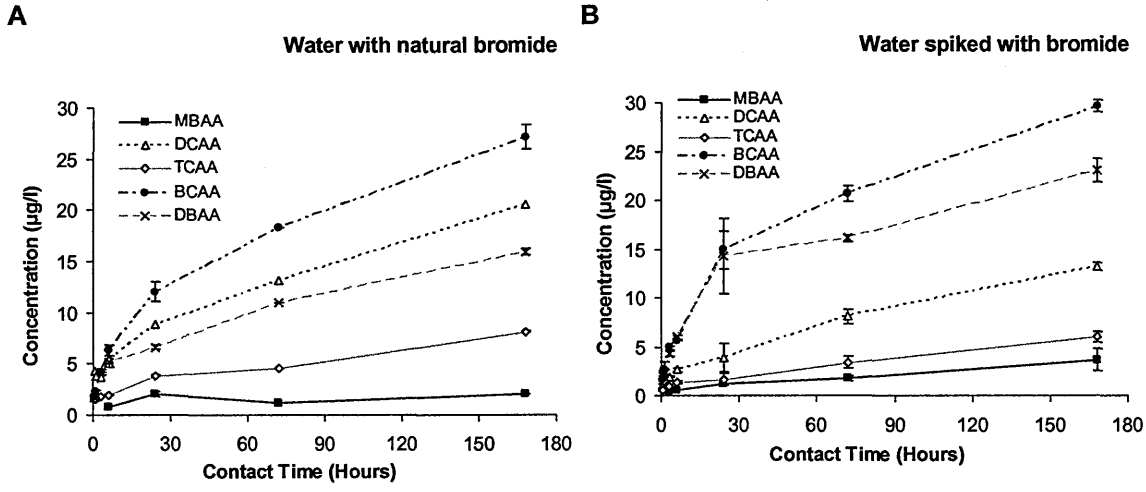


Figure 6.20: The concentrations of the individual HAA species at the various chlorination contact times for lowland water, under A) natural and B) spiked conditions. Error bars are the spread of the duplicate concentration measurement.

The relative distribution of the individual HAAs after 168 hour of contact, for the natural and spiked waters are illustrated in Figure 6.21.

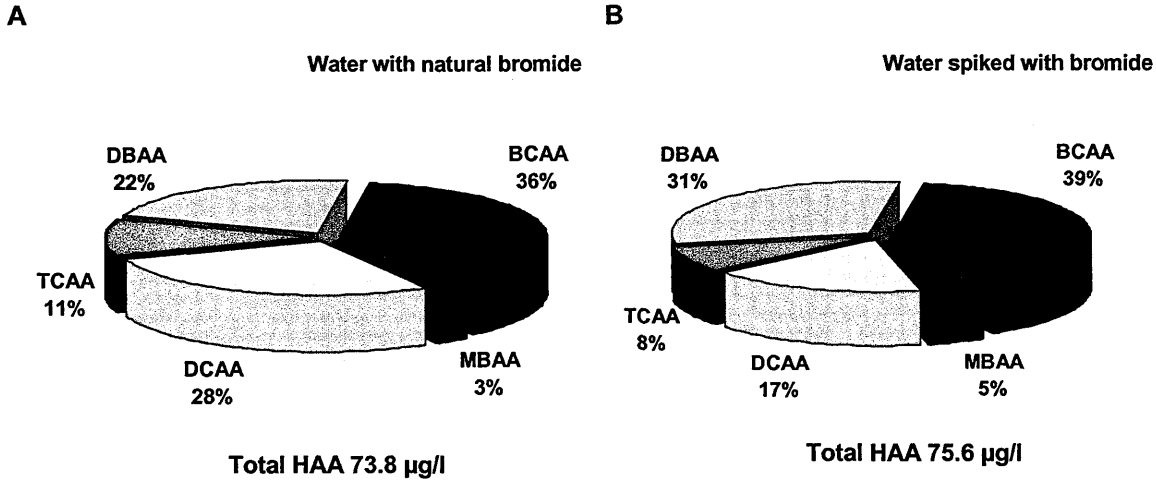


Figure 6.21: Pie charts showing the distribution of the HAAs after 168 hours of contact time, in lowland water, with under A) natural (206 µg/l) and B) spiked (406 µg/l) conditions.

6.4.3.6 Individual HAAs in upland water

The main HAAs formed in upland water, under the natural bromide content, were TCAA, DCAA and BCAA; while the other HAAs were not detected, probably because of the low levels of bromide present (34 µg/l). As anticipated, there was a significant shift in the concentration of the HAAs as a consequence of the addition of 200 µg/l of bromide. As shown by Figure 6.22, all five HAAs were quantifiable in the upland water after spiking.

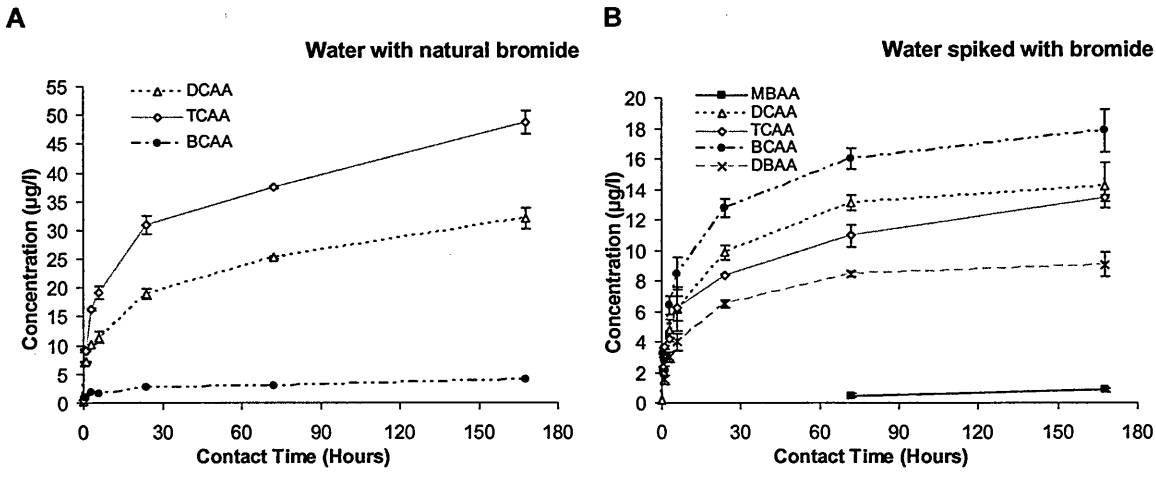


Figure 6.22: The concentrations of the individual HAA species at the various chlorination contact times for the lowland water, under A) natural and B) spiked conditions. Error bars are the spread of the duplicate concentration measurement.

In the spiked sample, after 168 hours of chlorination contact, the concentrations of TCAA and DCAA are greatly reduced, and their relative abundance fell from 57 to 24 % and 37 to 26 %, respectively. BCAA concentrations was significantly higher (4.4 times) while DBAA, which previously was not detected, was measured at 9.1 µg/l. MBAA concentration remained low (< 3.7 µg/l).

The pie charts for the natural and spiked upland water illustrate the change in the distribution of HAAs after 168 hours (Figure 6.23). The proportion of BCAA increased, while DBAA concentration increased to 16 %. The proportion of MBAA did not change.

A B

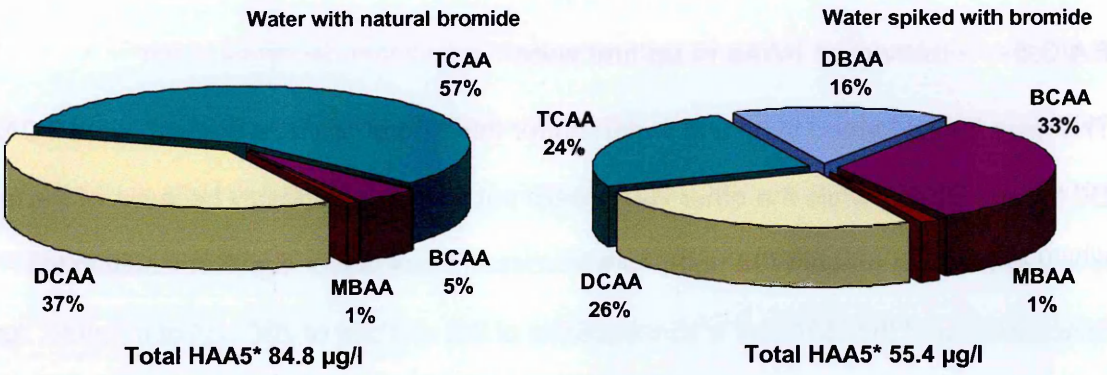


Figure 6.23: Pie charts showing the proportions of the HAAs after 168 hours of contact time, in upland water under A) natural (34 µg/l) and B) spiked bromide levels (234 µg/l).

6.4.4 A discussion on the influence of bromide ions on the formation of THMs and HAAs

Bromides (Br^-), regarded as a precursor to DBP formation, are inorganic ions that occur naturally in potable water, and can exhibit seasonal and geographical fluctuations (WHO, 2006). Bromide levels in water can increase because of sea water intrusion and seasonal droughts (Nokes *et al.*, 1999). Anthropogenic sources of bromides include pesticides, fuel additives and industrial effluent, but their contribution to the overall bromide levels is believed to be relative small (Magazinovic *et al.*, 2004). Bromide ions do not react directly with NOM but are oxidized with hypochlorous acid (HOCl) to form hypobromous acid (HOBr), as described by Equation 6.1 (Huang *et al.*, 2008; Parsons *et al.*, 2006a). Analogous to HOCl, HOBr also dissociates to hypobromide ions (OBr^-) as described by Equation 6.2.

$$Br^-_{(aq)} + HOCl \leftrightarrow HOBr + Cl^- \qquad \text{Equation 6.4}$$

$$HOBr \leftrightarrow H^+ + OBr^- \qquad \text{Equation 6.5}$$

In this study, the addition of bromide ions (200 µg/l) to each of the bulk waters increased the formation of the brominated THMs leading to an overall increase in THM4 concentrations. The addition of bromide ions also resulted in an increase in brominated

HAA species; however, in this case, there was a significant decrease in the concentrations of chlorinated HAAs. This did not have a large impact on the HAA5* concentrations in lowland water, but decreased the HAA5* concentrations in upland water, which resulted from a larger decrease in DCAA and TCAA and a smaller increase in the brominated species MBAA, BCAA and DBAA.

The increase in the brominated analogues was due the conversion of spiked bromide ions to hypobromous acid in the presence of hypochlorous acid, which in turn reacted with NOMs. The reaction rate for HOBr with NOM has been estimated to be 25 times stronger than HOCl (Duong *et al.*, 2003; Rathbun, 1996; Symons *et al.*, 1996; Uyak *et al.*, 2007a).

In excess chlorine (HOCl) and limited bromide conditions, as in natural upland water, the formation of $CHCl_3$ and $CHCl_2Br$ and chlorinated HAAs are favoured. Under higher bromide content and excess chlorine, as in natural lowland water and bromide-spiked upland water, all four THMs and five HAAs are formed. Increasing the bromide by a factor of two, in natural lowland water, has minimal influence on the HAA5* concentrations but increases THM4 levels. It also results in increased proportions of brominated THMs and HAAs.

These findings, for UK sources water samples, are consistent with those reported in the literature. Several studies have shown that high concentrations of bromide ions in the water shifts the distribution of HAAs and THMs to more brominated species, and can also lead to an increase in total THM and HAA concentrations (Chang *et al.*, 2001; Heller-Grossman *et al.*, 1993; Hong *et al.*, 2007; Nobukawa *et al.*, 2001; Uyak *et al.*, 2007a).

Different responses were observed for MBAA, DBAA and BCAA in each of the two waters on spiking. MBAA was least influenced by bromide addition in both waters, whilst DBAA, followed by BCAA, showed the greatest yield in upland water relative to lowland water. The bromide-rich HAAs were being preferentially formed, potentially suggesting a different

formation pathway for each of the HAAs. Singer and Reckhow (2010) have suggested that dihaloacetic acid pathway of formation is different to trihaloacetic acids.

However, the impact of bromination on total abundance of HAAs will vary depending on the number and species of HAAs measured. In this study, only five HAAs (MBAA, DCAA, TCAA, DBAA and BCAA) are quantified (HAA5*), however, as lowland water contains a higher level of bromide it could account for other more brominated species, such as TBAA, being present but unmeasured. As discussed earlier, MCAA could not be measured reproducibly; however, since it is included in the US regulated HAA5, its presence would have given a deeper understanding on the influence of bromide on the HAAs that are covered by legislation.

As bromide ions are naturally present in water systems and fluctuate seasonally, they need to be monitored regularly. The removal of such DBP precursor compounds, such as the use of granular activated carbon (GAC) technologies, could be used as part of a water company's control strategy to prevent the formation of THMs and HAAs.

6.4.5 Results of the investigation into the influence of reduced the water temperature on the formation of THMs and HAAs

As reported in Section 6.2, the baseline for chlorination was 20 °C and pH 7. The experiments were repeated with the pH maintained, but this time the temperature of the water was reduced to 7 °C during chlorination.

6.4.5.1 THM4

As can be seen from Figure 6.24, the THM4 concentrations, for both lowland and upland waters, were significantly lower when the water temperature was maintained at 7 °C. After 168 hours of contact time, the THM4 concentration in lowland water (50.5 µg/l) and upland water (34.0 µg/l) were significantly lower at 7 °C. At 20 °C, the THM4 concentration in lowland water was 89.4 µg/l, whereas in upland water it was 70.1 µg/l.

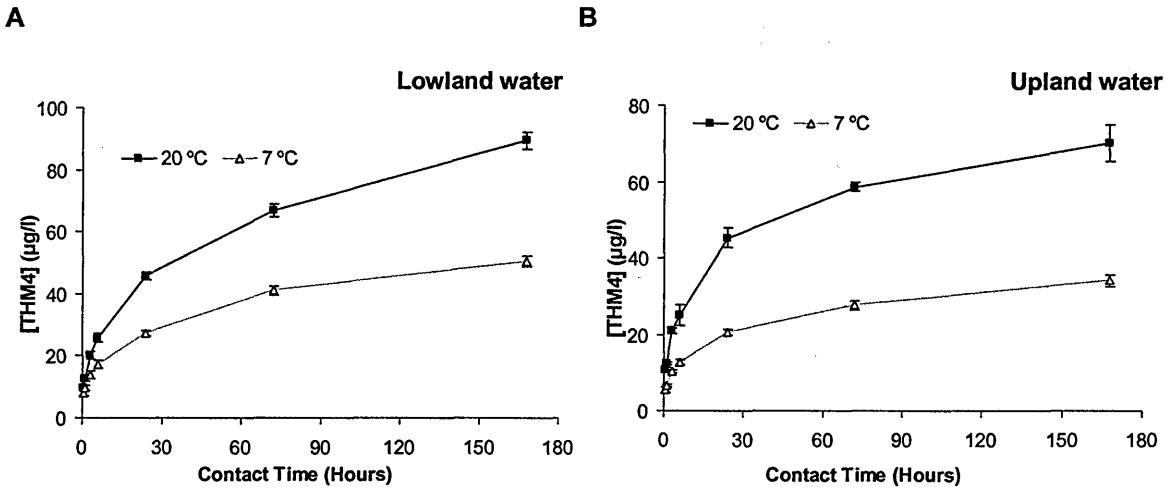


Figure 6.24: [THM4] at 7 °C and 20 °C, at pH 7, for A) lowland and B) upland water. Error bars are the cumulative error of the sum of the mean concentrations, n=6.

6.4.5.2 Individual THMs in lowland water

As expected, the concentrations of all four THMs were lower at 7 °C. The relative amounts of the individual THMs at the two temperatures were also different and are illustrated in Figure 6.25.

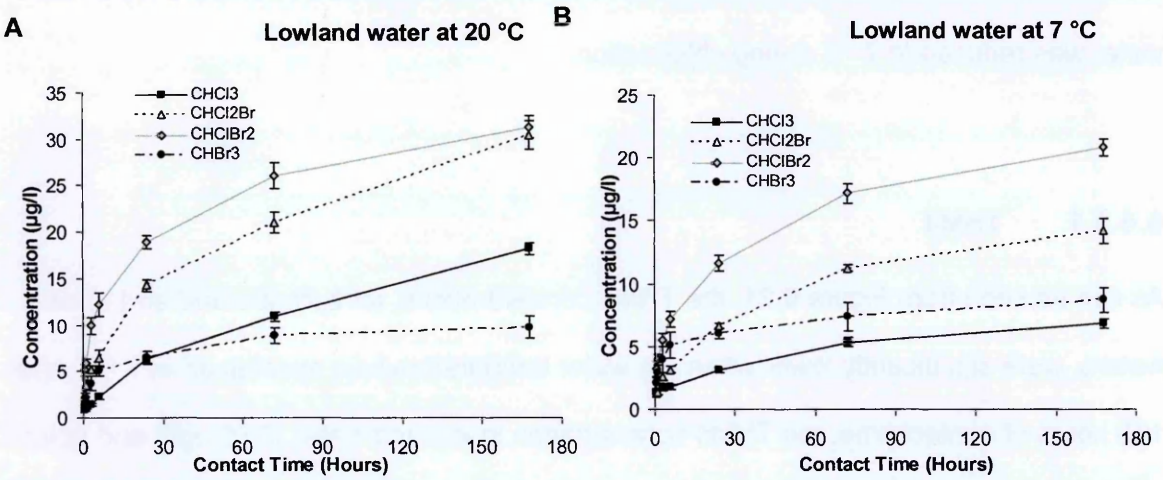


Figure 6.25: The concentrations of the individual THMs for lowland water at A) 20 °C and B) 7 °C. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

$CHCl_3$ and $CHCl_2Br$ were the most influenced by temperature, while $CHClBr_2$ and $CHBr_3$ were least influenced. After 168 hours of contact, the $CHCl_3$ concentration was 0.4 times lower while $CHCl_2Br$ levels reduced by half. $CHClBr_2$ and $CHBr_3$ levels were 0.7 and 0.9 times lower, respectively. As illustrated in Figure 6.26, the lower temperature resulted in an increase in the proportions of $CHClBr_2$ (from 35 to 42 %) and $CHBr_3$ (from 11 to 17 %).

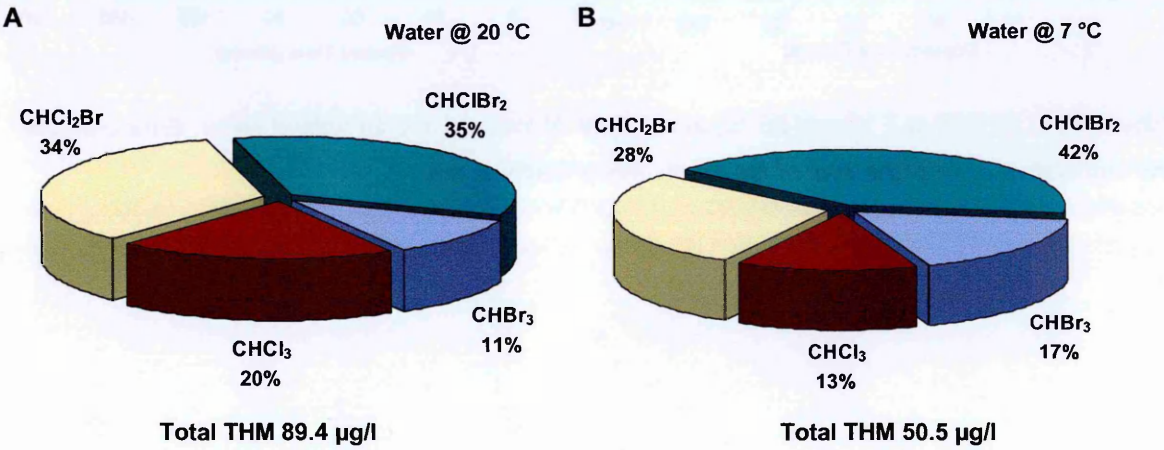


Figure 6.26: Pie charts showing the distribution of THMs after 168 hours of chlorine contact in lowland water at A) 20°C and B) 7°C.

6.4.5.3 Individual THMs in upland water

As reported earlier, $CHCl_3$ and $CHCl_2Br$ were the only two THMs detected in upland water. Figure 6.33 shows the concentrations of both these THMs at 20 and 7 °C.

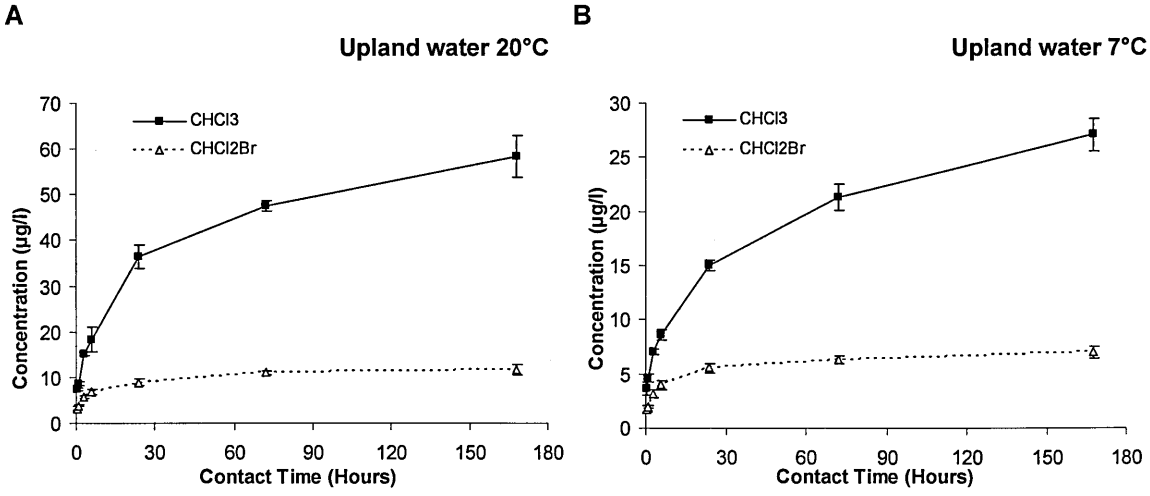


Figure 6.27: The concentrations of the THMs for upland water at temperature of A) 20 °C and B) 7 °C. Error bars are the standard deviation σ_{n-1} from the mean concentration, n=6.

After 168 hours of chlorination, at the lower water temperature, $CHCl_3$ levels were half of those at 20 °C; while $CHCl_2Br$ concentration was 0.6 times lower. Concentrations of $CHClBr_2$ and $CHBr_3$ were below the detection levels at both temperatures. The proportions of the THMs remained the same at both temperatures.

6.4.5.4 HAA5* and individual HAAs

Owing to an unexpected issue with the GC×GC-ToFMS data collection software, no chromatograms were collected for the samples injected by the autosampler. The experiments could not be repeated, as the samples were lost through evaporation over the weekend. Therefore, the influence of temperature on HAA formation could not be characterised. However, one would have expected a similar influence as for the THMs.

6.4.6 A discussion on the influence of water temperature on the formation of THMs and HAAs

This study has shown that a lower temperature results in lower concentrations of THMs formed in a given period of chlorination. This finding is consistent with the finding of Chapter 2 and those reported in the literature (El-Shafy *et al.*, 2000; Garcia-Villanova *et al.*, 1997; Nikolaou *et al.*, 2004b; Roccaro *et al.*, 2008; Toroz *et al.*, 2005). In Chapter 2, it was observed that THMs in Yorkshire Water's distribution system fluctuated owing to seasonal temperature variation with higher levels during the higher summer temperatures and vice versa. Nikolaou *et. al* (2004b) also reported that all four THMs increased with an increase in temperature, with chloroform showing the greatest increase. Roccaro *et. al* (2008), from experiments on water samples from a service reservoir in Italy, reported that an increase in temperature from 3 °C to 20 and 34 °C, caused an increase in THM4 concentration of approximately 1.6 and 2.1 times. It had also been previously reported that temperature will affect the reaction rate between NOM and chlorine during the formation of THMs and HAAs (Aysegul, 2003).

In this study, it was noted that brominated THMs were least influenced by temperature. This would seem to be consistent with a greater reaction rate for HOBr with NOM compared to the HOCl, as discussed in Section 6.4.4.

Although this study did not determine the influence of temperature on HAAs, previous publications have shown similar results to THMs. Dojlido *et al.* (1999) reported lower concentrations of HAA5 at lower temperatures in treated water samples in Warsaw, Poland. Bundy *et al.* (2005) also reported decreased HAA9 concentrations resulting from decreased temperatures (25 °C to 4 °C) in a kinetic study of treated water samples in USA.

Singer and Recknow (2010b) also reported the relative influence of temperature on certain THMs and HAAs. They noted that the formation of chloroform was more sensitive to temperature than DCAA formation, whist no clear relationship was found with TCAA formation. Singer *et al.* reported that at high temperatures DBPs, such as HAAs, degrade more quickly. As temperatures increase, certain DBPs would undergo abiotic reactions with chlorine faster, and can lead to a decrease in the concentration of certain DBPs in water (Singer *et al.*, 2010b).

6.4.7 Evaluating the validity of estimating HAA5* concentrations from THM4 concentrations

Owing to the complex nature of the DBP precursors, empirical models for the quantitation of DBPs are used to help guide decision-making in the drinking water industry. Srodes *et al.,* (2003) suggested that a 'statistically significant' correlation between THM and HAA concentrations would allow an estimate of the HAA concentration from THM concentration measurements. Such a system would be useful for quality control and monitoring of these compounds, as the analyses for HAAs is considerably more costly and time consuming compared to THM analyses . Hence, an investigation was undertaken to establish if such a correlation between HAA5* and THM4, at different pHs and bromide concentrations, existed in UK water samples; using the data obtained in this chapter. An evaluation with temperature was not possible because of the loss of the samples, as reported in Section 6.4.5.4.

6.4.7.1 Lowland water

As illustrated in Figure 6.28, a linear correlation exists between HAA5* and THM4 concentrations at all three of the pH conditions. The spiking of bromide (200 µg/l) to the water, at pH 7, also resulted in a linear correlation. An increase in THM4 concentrations linearly increases HAA5* concentrations. However, the slopes of the correlation were

different. The higher the pH, the higher the slope, whilst the addition of bromide has the greatest influence on the concentrations of the two DBPs.

As an example, in lowland water, at pH 8 and 20 °C, a THM4 concentration of 70 µg/l, would correlate to approximately 35 µg/l of HAA5*. At a reduced pH of 7, this would correlate to 55 µg/l of HAA5*. The addition of bromide (200 µg/l), at pH 7 and 20 °C, means that a THM4 concentration, at 70 µg/l, corresponds to a concentration of HAA5* at 30 µg/l.

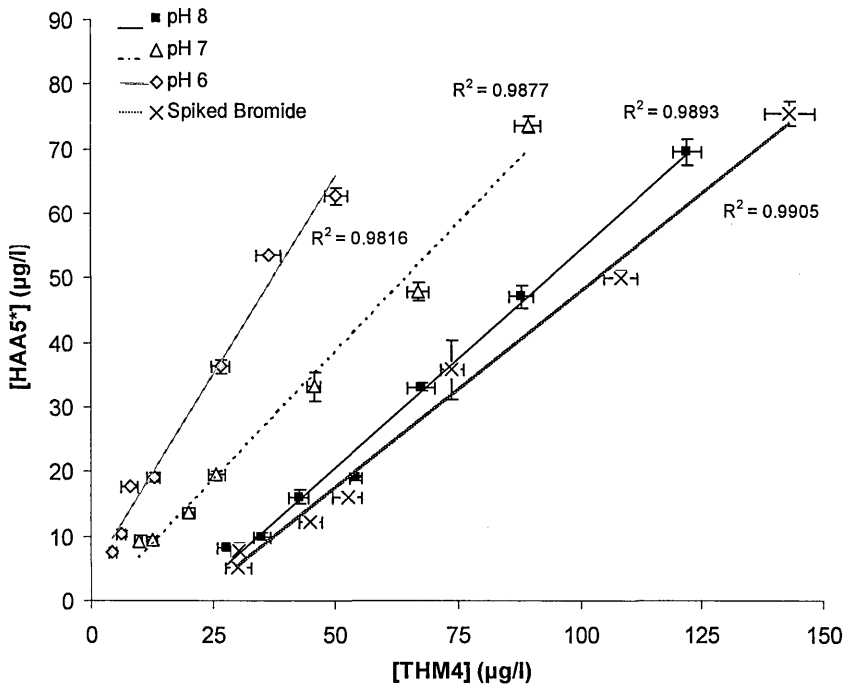


Figure 6.28: The correlation between [HAA5] and [THM4] for the lowland water source at the pH 6, 7 and 8 and [Br] addition. Error bars are the cumulative error of the sum of the mean concentration of the THM (n=6) and HAA (n=2).*

The parameters of the best-fit lines have been summarised in Table 5.6.

Table 6.6: Values of the slope, intercept and correlation for the HAA5* and THM4 in lowland water

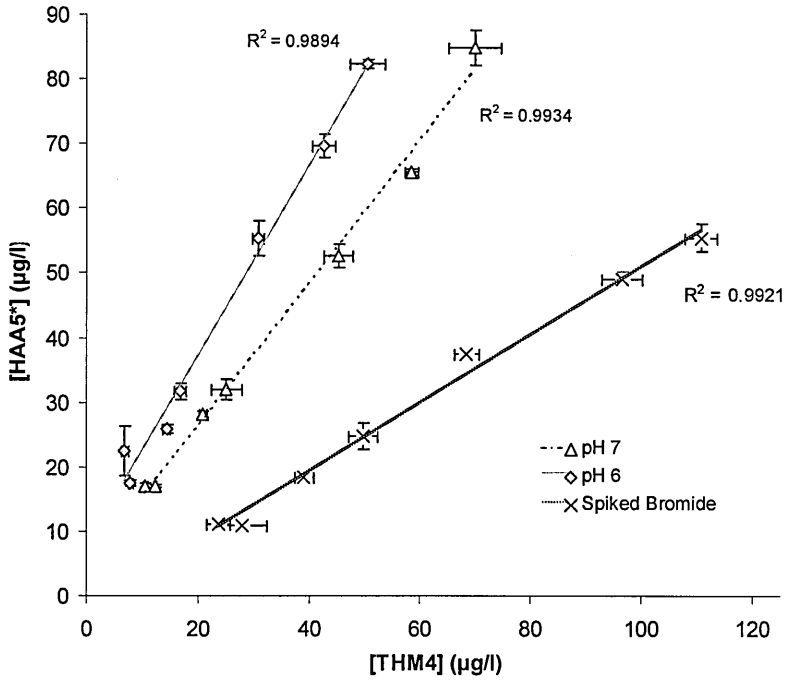
	Slope	**Y intercept**	**R^2**
pH 6	1.2213	4.3677	0.9816
pH 7	0.7948	-1.1609	0.9877
pH 8	0.6735	-13.08	0.9905
[Br] Addition	0.6104	-13.191	0.9893

6.4.7.2 Upland water

Clear linear correlations ($R^2 > 0.9894$) are also observed between HAA5* and THM4 concentrations, for pH 6 and 7 (Figure 6.29 A). The addition of bromide, at pH 7, had an influence on HAA5* and THM4 concentrations, with a greater slope than obtained at natural bromide levels and pH7. However, at pH 8, the relationship did not appear linear, however, a linear regression line was drawn for indication purposes only, as illustrated in Figure 6.29 B.

For example, in upland water, at pH 7 and 20 °C, a THM4 concentration of 40 µg/l, would correlate to approximately 50 µg/l of HAA5*. At the same pH and temperature, the addition of bromide (200 µg/l) means that a THM4 concentration at 100 µg/l corresponds with the same concentration of HAA5* (50 µg/l). The parameters of the best-fit lines have been summarised in Table 5.7.

A



B

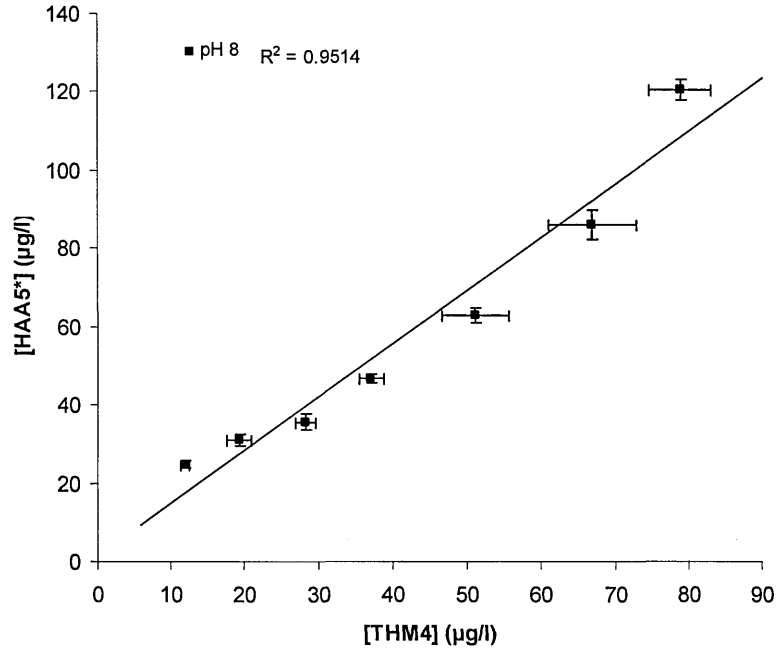


Figure 6.29: The correlation between [HAA5] and [THM4] for the upland water sources at A) pH 6 and 7, and [Br] addition and B) pH 8. Error bars are the cumulative error of the sum of the mean concentration of THM (n=6) and HAA (n=2).*

Table 6.7: Values of the slope, intercept and correlation for the HAA5* and THM4 in upland water

	Slope	Y intercept	R^2
pH 6	1.4706	7.813	0.9894
pH 7	1.1029	4.2037	0.9934
pH 8	1.3555[1]	1.3559[1]	0.9514[1]
[Br] Addition	0.5293	-1.9429	0.9921

[1] *values of a linear correlation line for indication purposes only.*

6.4.7.3 Discussion on the validity of estimating HAA5* concentrations from THM4 concentrations

Several studies have investigated the correlation between THMs and HAAs. Ates and colleagues reported a good correlation between THMs and HAAs with a R^2 value of 0.87 (n=29) in formation potential experiments (Ates *et al.*, 2007). Singer *et al.* (1995) have also reported high positive correlation coefficients between HAAs and THMs with an R^2=0.90 (Singer *et al.*, 1995). In a study by Nissinen *et al.* (2002), HAA6 correlated significantly with THM4 with a R^2=0.90 (n=30). Similarly, Villanuevaa and colleagues showed a "statistically strong correlation" between total THM and HAA concentrations with

an R^2 = 0.82 (n=18), in a subset of the dataset in which HAA concentrations were available (Villanueva *et al.*, 2003). Sérodes *et al.* (2003) also reported a moderate correlation between THM and HAA concentrations at different incubation temperatures (R^2= 0.75).

In a study of HAAs and THMs in the UK, Malliarou *et al.* (2005) found a good correlation at two geographically different regions (n=31 and n=29) but could find no correlation in another region (n=27) (Malliarou *et al.*, 2005). They also reported that the correlation of HAAs and THMs was linked to pH, temperature and free/total chlorine. In a more recent study on UK waters, Bougeard (2009) also reported a good correlation between THM4 and HAA9 (R^2 = 0.82) with the use of chlorine as a disinfectant, but found no correlation with the use of monochlorine as a disinfectant (n=11).

The correlation between THMs and HAAs in this study was generally very good and was found to be valid at the various pHs and on addition of bromide. THM4 concentrations could be used to predict HAA5* concentrations if conditions such as temperature, chlorination contact time and bromide levels are known. However, the use of THM levels as a good indicator for HAA levels could be premature. This is because these data can only be confidently applied to the standardised formation potential conditions for the two waters. A number of parameters can vary in the water samples and in the treatment processes. In addition, this study excludes other HAAs, such as the USEPA regulated MCAA, which would have an influence on the final correlation. The small size of the sample set would also suggest that over interpretation of the data should avoided. However, this work suggests that further studies should be undertaken to explore and investigate the correlation on a wider range of water samples under different conditions

Despite finding good correlation between HAAs and THMs, Sérodes, Bougeard and Malliarou also concluded that THM levels should not be used as a surrogate for HAAs; however, Villanueva suggested the opposite.

Several predictive models have been reported in the literature (Sadiq *et al.*, 2004). Using GC-μECD data, Bougeard (2009) investigated the chlorine decay model using the methodology adopted by Gang and colleagues (Gang *et al.*, 2002). She concluded that the model followed the general DBP formation trend, whereby pH had a greater impact in lowland water (Bougeard, 2009).

6.5 Conclusions

This study explored the influence of contact time, pH, bromide ion concentration and water temperature on the formation of THMs and HAAs during chlorination of treated water from lowland and upland sources in the UK. The results of this study were generally consistent with what has been reported in the literature. The conclusions of this Chapter are:

- The longer the chlorination contact time, the more THMs and HAAs that are formed until it is no longer chlorine limiting.
- Both individual THM and THM4 concentrations increased with an increase in pH from 6 to 8, in both lowland and upland waters. Under the formation potential conditions used in this study, it was noted that the lowland water would fail UK THM regulations at pH 8, if measured after 168 hours at 20 °C; but upland water would remain below the regulated limit at all three pH conditions, at the same temperature. The difference in THM4 concentrations between the two waters could be explained by the dissimilar NOM concentrations, NOM composition and bromide levels of the bulk waters.
- The HAA5* concentrations (MCAA excluded) in lowland water did not appear to have a strong dependence on pH. However, in upland water HAA5* increased with a rise in pH from 6 and 7 to 8. The differences in the characteristics of the bulk water samples may account for these observations. In contrast to THMs, there is less agreement in the literature on the influence of pH on HAA formation.

- The addition of bromide ions to each of the two waters increased the formation of the brominated THMs leading to an overall increase in THM4 concentrations. The proportions of the THMs was more significantly changed in the upland water samples.
- The addition of bromide ions also resulted in an increase in brominated HAA species; however, in this case, there was a significant decrease in the concentrations of chlorinated HAAs. This did not have a large impact on the HAA5* concentrations in lowland water, but decreased the HAA5* concentrations in upland water, which resulted from a decrease in DCAA and TCAA and an increase in the brominated species MBAA, BCAA and DBAA.
- A lower temperature results in lower concentrations of THMs formed in a given period of chlorination. Brominated THMs were least influenced by temperature.
- The influence of temperature on HAA concentrations was not investigated because of technical issues with the instrumentation; however, previous studies have shown similar trends to THMs.
- A correlation exists between THM4 and HAA5*, valid at various pHs and bromide concentrations. THM4 concentrations could be used to predict HAA5* concentrations if conditions such as temperature, chlorination contact time and bromide levels are known. However, owing to the number and complexity of parameters that influence their formation, the use of THM levels as a good indicator for HAA levels could be premature.
- Problems were identified in the measurement of MCAA. Several other studies have also reported problems in the measuring MCAA on a GC-μECD (Malliarou *et al.*, 2005; Reckhow *et al.*, 2008; Xie, 2001). This could be owing to poor extraction efficiency, poor derivatisation efficiency or more likely the loss of volatile MCAA methylester during sample handling.
- In contrast to other studies, problems were found in the measurement of DCAA in treated water samples. Since DCAA is one of the most abundant HAAs in many water

supplies, it needs to be accurately measured. Differences in concentrations measured on the GC-μECD and GC×GC-ToFMS led to the discovery of a co-eluting compound, which resulted in the GC-μECD overestimating the DCAA concentrations by up to 50 %.

- Through the use of the GC×GC-ToFMS, the co-eluting compound was identified as 1,1,1-trichloro-2-propanone (111-TCP). 111-TCP is a disinfection by-product belonging to the group haloketones, and had been reported in drinking water supplies (Golfinopoulos and Nikolaou, 2005).

- The co-elution of 111-TCP was resolved by changing the original SGE BPX5 column for a J&W DB 5.625 column on the GC-μECD, and will be utilised in Chapter 7. Other studies have used different non polar stationary phases, such as J&W DB1 and J&W DB5, for HAA analyses. Whether these phases separate the DCAA and 111-TCP better than SGE BPX5 would need to be established.

- GC×GC-ToFMS benefits from an increased chromatographic resolution and the use of the fragment ion (*m/z* 59), specific to the methyl ester, for quantitation and compound identification. The disadvantages are that it is more expensive, has higher running costs, and requires a significantly longer data processing time. Thus, the instrument is not ideal for the routine analyses of HAAs. Alternative, more affordable comprehensive chromatography solutions (GC×GC-μECD) are becoming more readily available and would have the advantage of both systems.

6.6 Further work

In the analyses of HAAs, the instrument component constitutes only 30 minutes of an overall sample preparation and analysis period of more than 6.5 hours. Whilst samples can be prepared in batches, any further developments of the method should examine how the efficiency of this process could be improved, without compromising on the quality of the results, allowing the technique to be viable for routine sample analysis.

In order to generate accurate multiple-regression models for UK water sources, a study should be performed on water samples over the range of parameters experienced at each of the water treatment plants. For this to be practical the improvements alluded to above would need to be implemented.

Based on the findings of this chapter, any further investigations should be performed to determine the influence of disinfection parameters on the formation of HAA9 rather than just HAA6, as undertaken in this study.

7. A study of the HAAs concentrations in various geographical locations across England

7.1 Introduction

As previously reported, haloacetic acids (HAAs) are disinfection by-products which are currently not regulated in the UK and Europe, but are under consideration (Cortvriend, 2008). Since they are currently not regulated, information on the range of concentrations found throughout the UK is limited. At the start of this research, only one study was found reporting the levels of HAAs in UK drinking water (Malliarou *et al.*, 2005). Malliarou *et al.,* found that the mean HAA9 concentration (DCAA, TCAA, MBAA, BCAA, DBAA and BDCAA), in three different geographical regions, ranged between 35 µg/l to 95 µg/l, with a maximum HAA9 concentration of 244 µg/l.

Learning the lessons from the previous chapters, in particular the importance of bromine concentrations on the distribution of HAAs formed, the aim of this study was to determine the concentrations of each of the nine HAAs, the total concentration of the nine HAAs (HAA9) and the US regulated HAA5, from thirteen sites within five water utility companies, across England.

The Drinking Water Inspectorate (DWI) has categorised England into six regions, namely: Central, Northern, Eastern, Thames, Southern and Western. The samples obtained from the five utility companies were from the Northern, Eastern and Central regions as shown in Figure 7.1. It should be noted that the aim of this study was only to survey the concentrations of HAAs found across three regions of England and did not examine the factors that influence the formation of HAAs across these regions.

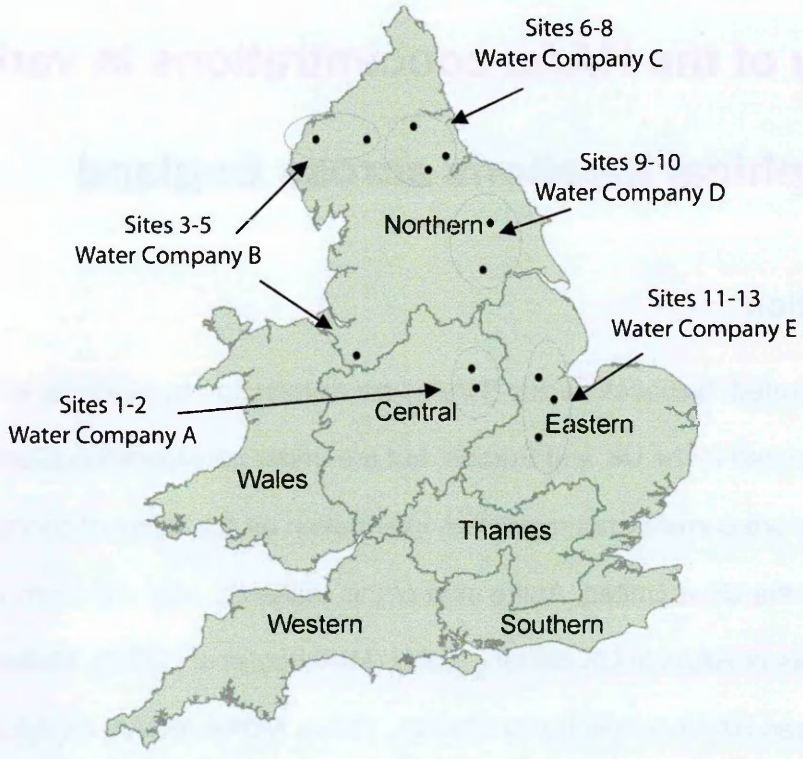


Figure 7.1: A map showing the locations of the 13 sampling sites and the water companies involved overlaid on a diagram, obtained from DWI (2009), showing the distribution of the regions.

7.2 Materials and methods

Duplicate clean plastic containers (40 ml) were sent to the five water companies for the collection of the water samples, at selected points in the treatment plants. The sampling was performed after disinfection but prior to the entry of the water into the distribution system. The samples were collected in February 2008 and sent to the laboratories at the Cranfield Water Sciences Institute, where they were stored at 5 °C. The sample preparation, extraction and derivatisation of the HAAs to their respective methyl esters were performed as reported in Chapter 3, within two weeks of sample receipt.

The derivatised samples were then sent to The Open University for analysis. The analyses were performed on the Agilent 6890 GC-μECD using a J&W DB-5.625 column, as previously described in Chapter 3 and discussed in Chapter 5. The analyses were performed within two week of sample preparation. GC×GC-ToFMS was not available for use during the period of this trial because of other commitments on the instrument.

However, having resolved the issues with the co-elution of contaminants with DCAA by the use of the J&W DB-5.625 column, it was decided to proceed with the study utilising only the GC-μECD.

7.3 Results

7.3.1 Confirmation of the validity of the MCAA concentration measurements

In the previous chapter, issues were raised on the reproducibility of MCAA concentrations. MCAA is important as it is one of the HAA species used to calculate the US regulated HAA5 concentration. A more systematic approach to the handling of samples, in particular the removal of processes that could result in the loss of volatile species, such as MCAA was therefore implemented.

A short study was conducted prior to the geographic trial to establish if these changes had resulted in an improvement in MCAA's reproducibility. Table 7.1, shows results from the analysis of a single lowland and upland water sample, analysed in duplicate, by each of the instrumental methods. As can be seen, there is good reproducibility for each duplicate analysis and a good agreement between the instrumental methods, for both water sources. The results for MCAA from analyses by GC-μECD (J&W DB 5.625) were therefore included in this study and the values for HAA5 and HAA9 concentrations could be reported.

Table 7.1: The concentrations of MCAA as obtained by GC-μECD (SGE BPX 5), GC-μECD (J&W DB 5.625) and GC×GC-ToFMS (SGE BPX5 and SGE BPX50).

	Lowland Water (μg/l)	Upland Water(μg/l)
GC-μECD (BPX 5)	36.50 ± 6.34	22.08 ± 1.44
GC-μECD (J&W DB 5.625)	33.90 ± 3.90	21.00 ± 1.22
GC×GC-ToFMS (SGE BPX5 and SGE BPX50	36.88 ± 4.25	21.26 ± 1.15

Duplicate analyses performed for each method.

7.3.2 Results and discussion of the study

An example chromatogram of a water sample (from Site 12) is shown in Figure 7.2. Visual inspection of the chromatogram showed the presence of most of the HAA peaks, as well as a number of endogenous non-HAA peaks. Although some of these endogenous peaks were of greater intensity, all nine HAA peaks and the IS were clearly resolved from these peaks.

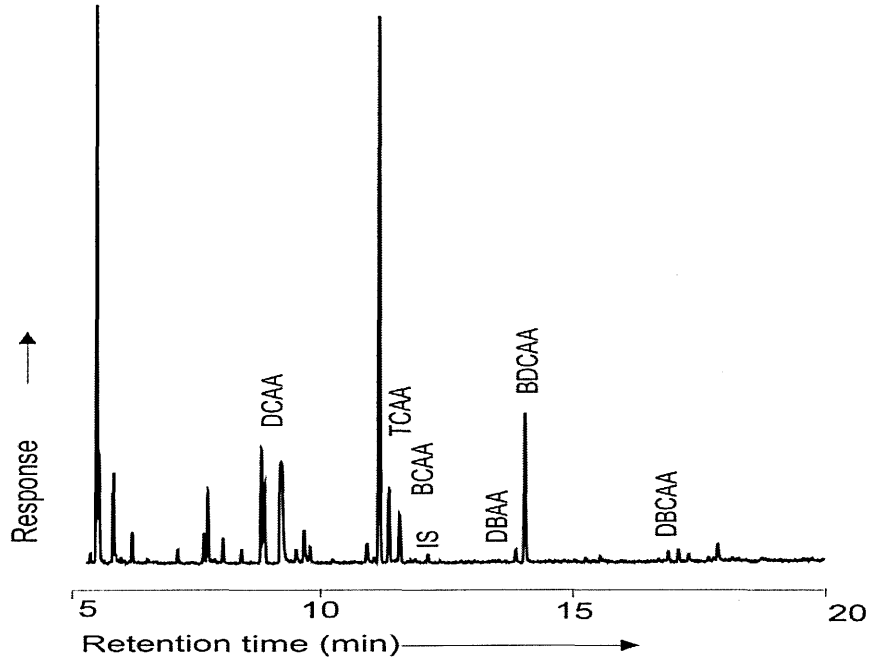


Figure 7.2: Chromatogram of a derivatised water sample from Site 12, obtained by the GC-μECD.

For each sample, good reproducibility was obtained for the two duplicate analyses, with an analytical precision of < 10 % of the measured value observed throughout. It has been previously reported that: MCAA had an LOD of 0.3 μg/l; MBAA, TCAA, DBAA and TBAA had an LOD of 0.2 μg/l; whilst DCAA, BCAA, BDCAA and DBCAA had an LOD of 0.1 μg/l.

The mean results obtained for each of the HAAs, at each of the sites, is summarised in Table 7.2, along with the HAA5 and HAA9 values. HAA5 is a summation of the mean concentrations of the five US regulated HAAs: MCAA, MBAA, DCAA, TCAA and DBAA. Whereas, HAA9 contains HAA5, as well as BCAA, BDCAA, DBCAA, and TBAA. The errors reported for HAA5 and HAA9 concentrations are cumulative errors.

Table 7.2: Distribution of the mean concentrations of individual HAAs, HAA5 and HAA9 from the 13 sample sites across England.

Site	Water Company	DWI Region	DCAA µg/l	TCAA µg/l	BCAA µg/l	DBAA µg/l	BDCAA µg/l	DBCAA µg/l	TBAA µg/l	HAA5 µg/l	HAA9 µg/l
1	A	Central	3.6	1.5	3.9	3.0	2.2	1.7	0.5	8.7 ± 0.4	17.0 ± 0.5
2	A	Central	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	-	-
3	B	Northern	7.2	5.7	2.0	0.4	1.3	0.2	< LOD	13.2 ± 0.3	16.6 ± 0.3
4	B	Northern	14.0	18.1	3.2	0.4	3.6	0.3	0.2	32.4 ± 0.4	39.7 ± 0.4
5	B	Northern	10.5	5.2	2.4	0.3	1.3	0.2	< LOD	16.0 ± 0.1	19.9 ± 0.1
6	C	Northern	< LOD	1.6	4.5	1.5	0.5	1.6	0.5	3.1 ± 0.4	10.2 ± 0.5
7	C	Northern	6.4	4.2	3.0	1.0	2.3	0.7	< LOD	11.6 ± 0.4	17.7 ± 0.5
8	C	Northern	18.5	9.4	1.9	< LOD	0.9	< LOD	< LOD	27.9 ± 1.4	30.7 ± 1.4
9	D	Northern	14.3	4.0	2.3	0.3	0.6	< LOD	< LOD	18.6 ± 0.4	21.4 ± 0.4
10	D	Northern	1.4	0.2	2.2	3.8	0.5	1.0	0.8	5.4 ± 0.1	10.0 ± 0.2
11	E	Eastern	2.0	0.4	2.7	2.9	0.7	1.0	0.4	5.3 ± 0.4	10.0 ± 0.5
12	E	Eastern	3.2	0.7	4.3	5.7	1.0	1.8	1.2	9.6 ± 0.1	17.9 ± 0.1
13	E	Eastern	0.7	< LOD	0.5	0.9	< LOD	0.2	0.2	1.7 ± 0.1	2.5 ± 0.1

MCAA < LOD in all 13 Sites and MBAA only detected in Site 1 at 0.5 µg/l.

Individual HAA concentrations are the mean of duplicate samples.

The error values for HAA5 and HAA9 concentrations are cumulative.

If we review the distribution of the individual HAAs in their chromatographic elution order, then we can observe the following:

- MCAA was not detected above the instrument detection limits at any of the 13 sites analysed.
- MBAA was observed only at Site 1, at a very low concentration of 0.5 µg/l.
- DCAA was most abundant in Sites 4, 5, 8 and 9, with Site 8 having the highest concentration of 18.5 µg/l.
- TCAA was most abundant at Site 4, at a concentration of 18.1 µg/l.
- BCAA levels found to be most abundant at Sites 1, 6 and 12, with the highest concentration being 4.5 µg/l.
- DBAA, was found to be the most abundant at Sites 10, 11 and12, with the highest concentration being 5.7 µg/l.
- BDCAA was most abundant at Site 1, 4, and 7, with the highest concentration being 3.6 µg/l.
- DBCAA was not detected above the instrument detection limits at Sites 2, 8 and 9 sites, with the highest concentration being 1.8 µg/l at Site 12.
- TBAA was not detected above the instrument detection limits at six sites, with the highest concentration being 1.2 µg/l at Site 12.

If we review the distribution of the HAA5 and HAA9 concentrations across the sites, then we can observe the following:

- Site 2 did not contain any HAAs above the instrument detection limits.
- Site 4 contained the highest HAA5 (32.4 µg/l) and HAA9 (39.7 µg/l) concentrations.
- Site 8 had second highest HAA5 and HAA9 concentrations at 27.9 µg/l and 30.7 µg/l, respectively.
- Site 13 had the second lowest HAA5 and HAA9 concentrations at 1.7 µg/l and 2.6 µg/l, respectively.

- If we consider the ratio of HAA9 / HAA5 at each of the sites, HAA9 is between 1.1 (Sites 8 and 9) and 3.3 (Site 6) greater than HAA5.
- If we consider the magnitude of HAA9 - HAA5 at each of the sites, HAA9 is between 8.3 µg/l (Sites 1 and 12) and 0.8 µg/l (Site 13) greater than HAA5.

Overall, the mean HAA5 concentration was 11.8 µg/l and mean HAA9 concentration was 16.5 µg/l across the 13 sites from the 5 water utilities in the 3 regions of England.
If we review the distribution of the HAA5 and HAA9 concentrations across the water companies, we can observe the following:

- Water Company B had the highest levels of HAA5 from its three sites (13.2 – 32.4 µg/l; mean HAA5 - 20.5 µg/l),
- Water company C had HAA5 concentrations ranging from 3.4 – 27.9 µg/l (mean HAA5 – 14.2 µg/l).
- The HAA5 concentrations in water company D ranged from 5.4 - 18.6 µg/l (mean HAA5 - 12.0 µg/l)
- Only one of the two sites in Water Company A contained any HAAs, with a HAA5 concentration of 8.7 µg/l.
- Water Company E had the lowest HAA5 concentrations across its three sites (1.7 - 9.6 µg/l; mean HAA5 - 5.5 µg/l).

Malliarou *et al.* (2005) undertook a study to measure the concentrations of HAAs in England and Wales. The samples were taken in the summer from across the Northern, Eastern and Western regions. MCAA could not be measured because of analytical issues and DBAA, DBCAA and TBAA were not detected above their limit of detection. The authors were therefore unable to report HAA5 concentrations and instead reported that the mean total HAA concentration (DCAA, TCAA, MBAA, BCAA, DBAA and BDCAA), from thirty samples, in each of three regions, ranged between 35.1 µg/l to 94.6 µg/l, with a maximum total HAA concentration of 244 µg/l. Their study also found that DCAA and TCAA were the most abundant HAAs with mean concentrations of 9.1 - 39.9 and 12.7 -

29.3 µg/l, respectively, for the 3 regions. The other four HAAs were each found at concentrations below 9.2 µg/l. In this study, DCAA and TCAA were consistently the most abundant in the Northern region, whereas in the other two regions (Central and Eastern) BCAA, DBAA and DCAA were the most abundant, but at much lower concentrations than in the Northern region. The higher values reported by Malliarou *et al.* (2005) are likely to be because of the fact that the samples were collected in the summer when the NOM, bromide ion concentration and water temperatures would have been higher.

A more recent study by Graham *et al.,* (2009), reported that the HAA5 concentrations, from three water supplies in England, were found to be below 41 µg/l in all four seasons. In their study, DCAA and TCAA were the major species in one utility, BDCAA and TCAA and BCAA and DBAA were the dominant species in the other two utilities, respectively.

7.4 Conclusions and future work

The results of this work showed that the total HAA5 across thirteen sites in England, in February 2008, had concentrations well below the US regulated levels of 60 µg/l. The highest HAA5 concentration was 32.4 µ/l and HAA9 concentration was 39.7 µg/l. TCAA and DCAA were present at the highest concentration in this study, whilst MCAA and MBAA were least dominant. BCAA and DBAA were most abundant in some sites, however, their concentrations were always found below 5.7 µg/l. The concentrations of the individual HAAs varied across the study, which was probably because of the different initial water conditions (based on geography and geology of the area) and treatments procedures in the sites.

Further work needs to be performed to assess the HAA levels of these water samples during the different seasons, as one might predict that HAA levels would increase during the warmer summer months. Investigations to measure the HAA concentrations across other regions of the United Kingdom should also be performed.

Having resolved the issue with DCAA concentration measurement by GC-μECD through the selection of the most appropriate stationary phase for the samples being analysed, there does not appear to have been an issue with the accuracy of the HAA concentrations measured. However, it would be recommended in future studies to use either comprehensive chromatography (GC×GC-ToFMS or GC×GC-μECD) or laboratory fortified water samples for each batch of analyses at each of the sites, as recommended by USEPA 552.3 (2003). This would eliminate the possibility of any co-elution of contaminant peaks with the HAAs of interest. The comprehensive chromatography solution, particularly GC×GC-μECD, is becoming increasingly affordable with the introduction by a number of suppliers of capillary flow technology (CFT), which enables flow modulation without the need of cryogens and enables existing laboratory systems to be upgraded. This approach attempts to prevent any chromatographic issues arising, whereas the use of spiked water samples allows for corrections to be made to existing data. Trade-offs would need to be made between capital equipment costs associated with comprehensive chromatography and the additional time/consumable cost associated with the additional number of samples that would need to be run to enable accurate corrections to be made.

As concluded in Chapter 6, the most time consuming component of the analysis is the sample preparation. Any development in improving the efficiency of the HAA extraction / derivatisation process would provide significant benefits in terms of time saving, sample throughput and inevitable cost. Such developments are more like to result in the method being applied for routine analysis.

8. Conclusions

This final chapter considers the outcomes of the project presented within this thesis in the context of the original aims.

Potable water distribution systems are a dynamic environment requiring constant monitoring of the levels of contaminants, such as THMs and HAAs, to ensure the highest quality and that regulatory standards are met. The monitoring of specific DBPs is not typically continuous, as the current industrial practice is manual sample collection, at regular intervals and at known locations, which are then sent to specialist analytical laboratories for analysis.

Both THMs and HAAs are toxic and hence their total concentrations are regulated in the US. THMs are volatile compounds and as a result would be suitable for near-real time analysis using methods investigated in this thesis. HAAs are non volatile and require complex sample preparation and derivatisation prior to chromatographic analysis. As a result, only THM concentrations are regulated in the UK and only one study of the HAA concentrations in treated UK waters had been published at the start of this research.

HAAs are considered as high priority compounds for potential regulation in the near future and are listed for future regulation in the EU Water Directive. In order to prepare for this regulation, water companies are taking a proactive approach to assess the most appropriate methodology for the analysis of HAAs in their water samples.

This PhD project was undertaken between The Open University, Yorkshire Water Services Ltd and Cranfield Water Science Institute to evaluate if suitable analytical methods, that utilised mass spectrometers as the detector, could be developed, optimised and have sufficient performance for the analysis of THMs and HAAs in UK water samples.

Prior to commencing the developments, a review of the temporal variations in THM concentrations and other parameters in YWS's distribution system was undertaken.

8.1 Temporal variations in THM concentrations and parameters relevant to DBP formation in YWS's distribution system

This study undertook a detailed analysis of selected sites in the YWS's potable water distribution system from 1998 - 2007 and has shown that it is a highly dynamic environment. It showed that the concentrations of THM4, in some of the service reservoirs, approached the regulated levels for the period between June 2006 and June 2007. The data also showed that they fully complied with their legal obligation, between January 2000 and June 2007, and maintained the THM4 concentration below 100 µg/l. The data has also provided a valuable insight into the temporal variations in many of the parameters that are important in the formation of disinfection by-products. These findings provided further evidence for the need to develop analytical methods that could be applied to a near-real time monitoring system.

8.2 Development and optimisation of methods for the analysis of THMs

HS-GC-MS, HS-SPME-GC-MS and HS-GC-µECD were evaluated in terms of their suitability for near-real time monitoring of THMs. Their analytical performances, in terms of their linearity, accuracy, reproducibility and detection limits, were characterised and evaluated against existing methods (LLE-GC-µECD). The conditions for headspace sampling were also optimised prior to characterisation. Based on the analytical performance and practical considerations both the HS-GC-MS and HS-SPME-GC-MS are both proposed to be viable for such a monitoring system, if an affordable instrument becomes available. Before any such system is implemented, further work would be required to comply with the provisions required by the DWI for on-line monitoring.

8.3 Development and optimisation of methods for the analysis of HAAs

Prior to the commencement of this thesis, only one study had reported measurements for HAA concentrations in UK potable water sources. A range of chromatographic methods were evaluated for their suitability for the analysis of HAAs, namely: GC-μECD, GC-MS (in electron impact ionisation mode), GC-MS (in chemical ionisation mode) and comprehensive chromatography (GC×GC-ToFMS). The chapter also investigated the influence of modified GC-μECD instrument parameters on its performance. Apart from GC-MS(EI), the performance of the methods developed, in terms of their linearity, repeatability, accuracy and detection limits, were equivalent to those used in regulatory laboratories.

It was concluded that the optimised GC-μECD method was the simplest and most sensitive technique, with slightly superior analytical accuracy and repeatability to the GC×GC-ToFMS. The comprehensive chromatography solution was also shown to possess good analytical performance. Both systems were therefore used to evaluate the formation potentials of the individual HAAs and the GC-μECD was used to study HAA concentrations present in water samples from around the UK.

8.4 A study measuring the formation potential of THMs and HAAs in UK waters

This study explored the influence of contact time, pH, bromide ion concentration and water temperature on the formation of THMs and HAAs during chlorination of treated water from lowland and upland sources in the UK. It utilised the optimised methods developed earlier. The results obtained were generally consistent with those reported in the literature and the findings from the study are summarised as:

- The longer the chlorination contact time, the more THMs and HAAs that are formed.

- Both individual THM and THM4 concentrations increased with an increase in pH from 6 to 8, in both lowland and upland waters. The HAA5* concentrations (MCAA excluded) in lowland water did not appear to have a strong dependence on pH. However, in upland water HAA5* increased with a rise in pH from 6 and 7 to 8.
- The addition of bromide ions to each of the two waters increased the formation of the brominated THMs leading to an overall increase in THM4 concentrations. The distribution of the THMs was more significantly changed in the upland water samples. It also resulted in an increase in brominated HAA species; however, in this case, there was a significant decrease in the concentrations of chlorinated HAAs. This did not have a large impact on the HAA5* concentrations in lowland water, but decreased the HAA5* concentrations in upland water.
- A lower temperature results in lower concentrations of THMs formed in a given period of chlorination. Brominated THMs were least influenced by temperature.
- A correlation exists between THM4 and HAA5*, valid at various pHs and bromide concentrations. THM4 concentrations could be used to predict HAA5* concentrations if conditions such as temperature, chlorination contact time and bromide levels are known. However, owing to the complexity, its use would be premature without further evaluation.
- As reported in other studies, problems were identified in the measurement of MCAA. Differences in DCAA concentrations measured on the GC-μECD and GC×GC-ToFMS led to the discovery of a co-eluting compound, which resulted in the GC-μECD overestimating the DCAA concentrations by up to 50 %. The co-elution of 111-TCP was resolved by changing the original SGE BPX5 column for a J&W DB 5.625 column on the GC-μECD.
- GC×GC-ToFMS has previously not been reported in literature for the analysis of HAAs in treated waters. The disadvantages of GC×GC-ToFMS are that it is more expensive, has higher running costs, and requires a significantly longer data processing time. Thus, the instrument is not ideal for the routine analyses of HAAs. Alternative, more

affordable comprehensive chromatography solutions (GC×GC-μECD) are becoming more readily available and would have the advantage of both systems.

8.5 A study of the HAAs concentrations in locations across England

As only one published study had reported measurements for HAA concentrations in UK potable water sources, this study determined the concentrations of each of the nine HAAs, the total concentration of the nine halogenated HAAs (HAA9) and the US regulated HAA5, from thirteen sites within five water utility companies, across England using the optimised analytical method developed. The total HAA5 concentration across thirteen sites in England, in February 2008, were well below the US regulated levels of 60 μg/l. TCAA and DCAA were present at the highest concentration in this study, whilst MCAA and MBAA were least dominant. BCAA and DBAA were most abundant in some of the sites. The concentrations of the individual HAAs varied across the study, which was probably because of the different initial water conditions (based on geography and geology of the area) and treatment procedures at the sites.

8.6 Concluding remarks

The project has succeeded in its overall aims to develop, optimise and apply new and existing analytical protocols for the analysis of THMs and HAAs from UK water sources. For the analysis of THMs, HS-GC-MS, HS-SPME-GC-MS and HS-GC-μECD were developed and optimised. The analytical performance of these methods (in terms of linearity, repeatability, accuracy and detection limits) was as good as regulatory methods (LLE-GC-ECD). The project concluded that HS-GC-MS and HS-SPME-GC-MS are both viable for near-real time monitoring, if a portable GC system became available.

The suitability of GC-MS(EI), GC-MS(ECNI), GC×GC-ToFMS and GC-μECD for HAA concentration measurements was also evaluated. GC×GC-ToFMS and GC-MS(ECNI)

have previously not been reported in literature for the analysis of HAAs in water samples. Apart from GC-MS(EI), the analytical performance of the methods developed were equivalent to those used in regulatory laboratories.

HS-GC-MS, GC-μECD and GC×GC-ToFMS were then utilised to determine the influence of a series of parameters on the formation potential of THMs and HAAs in upland and lowland water samples. GC-μECD was also applied to the determination of HAA concentrations in treated water samples from geographically different sources in the UK. The total HAA5 concentration across thirteen sites in England, in February 2008, had concentrations well below the US regulated levels of 60 μg/l.

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Appendices

List of Appendices

Appendix 1 - Tables

Table A.1: The chemical parameters that are currently regulated in the UK (DWI, 2000)

Parameter	Value	Unit
Acrylamide	0.10	µg/l
Antimony	5.0	µg/l
Arsenic	10	µg/l
Benzene	1.0	µg/l
Benzo(a)pyrene	0.010	µg/l
Boron	1.0	mg/l
Bromate	10	µg/l
Cadmium	5.0	µg/l
Chromium	50	µg/l
Copper	2000	µg/l
Cyanide	50	µg/l
1,2-dichloroethane	3.0	µg/l
Epichlorohydrin	0.10	µg/l
Fluoride	1.5	mg/l
Lead	10	µg/l
Mercury	1.0	µg/l
Nickel	20	µg/l
Nitrate	50	mg/l
Nitrite	0.50	mg/l
Pesticides	0.10	µg/l
Pesticides - Total	0.50	µg/l
Polycyclic aromatic hydrocarbons	0.10	µg/l
Selenium	10	µg/l
Tetrachloroethene and Trichloroethene	10	µg/l
Trihalomethanes - Total	100	µg/l
Vinyl chloride	0.50	µg/l

Table A.2: The indicator parameters that currently are required to be monitored in the UK (DWI, 2000).

Parameter	Parametric Value	Unit
Aluminium	200	µg/l
Ammonium	0.50	mg/l
Chloride	250	mg/l
Clostridium perfringens (including spores)	0	number/100 ml
Colour	Acceptable to consumers and no abnormal change	
Conductivity	2 500	µS cm^{-1} at 20°C
Hydrogen ion concentration	≥6.5 and ≤9.5	pH units
Iron	200	µg/l
Manganese	50	µg/l
Odour	Acceptable to consumers and no abnormal change	
Oxidisability	5.0	mg/l O_2
Sulphate	250	mg/l
Sodium	200	mg/l
Taste	Acceptable to consumers and no abnormal change	
Coliform bacteria	0	number/100 ml
Total organic carbon (TOC)	No abnormal change	
Turbidity	Acceptable to consumers and no abnormal change.	

Table A.3: Radioactivity parameters that are currently required to be monitored in the UK (DWI, 2000).

Parameter	Parametric Value	Unit
tritium	100	Becquerel/l
total indicative dose	0.10	mSv/year

Table A.4: The physicochemical properties of the four THMs.

IUPAC Name	Common name	Chemical formulae	Acronyms used in literature	Molecular mass [1, 5] (g/mol)	Melting point [5] (°C)	Boiling point [1, 5] (°C)	Vapour pressure [1, 5] (kPa)	Henry's constant [1, 4] (Pa m^3/mol)	Solubility in water [1, 4] (g/l)	Density [1, 2, 5] (g/ml)
Trichloromethane	Chloroform	$CHCl_3$	TCM, CF	119.38	-64	61	21.3 (20 °C)	440	0.8 (25 °C)	1.49
Bromodichloro methane		$CHCl_2Br$	BDCM	163.83	-57	90	6.7 (20 °C)	160	0.3 (30 °C)	1.98
Dibromochloro methane		$CHClBr_2$	CDBM	208.28	-20	120	2.0 (10 °C)	86	0.1 (30 °C)	2.45
Tribromomethane	Bromoform	$CHBr_3$	TBM, BF	252.73	8.3	149	0.8 (25 °C)	54	3.2 (25 °C)	2.78

IUPAC - International Union of Pure and Applied Chemistry

References:

[1] *Howard,(1990)*
[2] *International Program for Chemical Safety (2000)*
[3] *World Health Organisation, (2004a)*
[4] *Uyak et al., (2007c)*
[5] *Lide, (2004)*

Table A.5: The physicochemical properties of the nine HAAs.

IUPAC Name	Acronym	Chemical Formulae	Molecular mass [1] (g/mol)	Melting point [1] (°C)	Boiling point [1] (°C)	Density [1] (g/ml)	Molecular mass of ester [2, 3] (g/mol)	Boiling point of ester [2, 3] (°C)
Monochloroacetic acid	MCAA	$CH_2ClCOOH$	94.49	63.0	189.3	1.40	108.52	129.5
Monobromoacetic acid	MBAA	$CH_2BrCOOH$	138.94	50.0	208.0	1.93	152.97	132.0
Dichloroacetic acid	DCAA	$CHCl_2COOH$	128.94	13.5	194.0	1.56	142.96	142.9
Trichloroacetic acid	TCAA	CCl_3COOH	163.38	57.5	196.5	1.63	177.41	167.5
Bromochloroacetic acid	BCAA	$CHClBrCOOH$	173.39	29.5	215.0	1.98	187.42	174.0
Dibromoacetic acid	DBAA	$CHBr_2COOH$	217.84	49.0	129.0	n/k	232.87	195.0
Bromodichloroacetic acid	BDCAA	$CCl_2BrCOOH$	207.83	n/k	n/k	n/k	221.87	n/k
Dibromochloroacetic acid	DCBAA	$CClBr_2COOH$	252.39	n/k	n/k	n/k	266.35	n/k
Tribromoacetic acid	TBAA	CBr_3COOH	296.74	129.0	245.0	n/k	310.76	225.0

IUPAC - International Union of Pure and Applied Chemistry.
Esters - As HAAs are not GC amenable, they must first be derivatised to their methyl esters for analysis.
n/k - not know, data not available.

References

[1] *Lide,(2004)*
[2] *Howard,(1990)*
[3] *World Health Organisation (2004a)*

Table A.6: The advantages and disadvantages of different types of disinfectants and the respective DBPs formed (CCC, 2003; WHO, 2006).

Disinfectant	Advantages	Disadvantages	Disinfection by-product
Chlorine Gas	▪ Highly effective against most pathogens ▪ Provides "residual" protection required for drinking water ▪ Operationally the most reliable ▪ Generally the most cost-effective option	▪ By-product formation ▪ Special operator training needed ▪ Additional regulatory requirements ▪ Not effective against Cryptosporidium	THMs, HAAs, chlorates, carboxylic acids, aldehydres, ketones, ketoacids
Chloramines	▪ Reduced formation of THMs, HAAs ▪ More stable residual than chlorine ▪ Excellent secondary disinfectant	▪ Weaker disinfectant than chlorine ▪ Requires shipments and use of ammonia gas or compounds ▪ Toxic for kidney dialysis patients and tropical fish	Acetonytrile, ketones, chloramines
Ozone	▪ Produces no chlorinated THMs, HAAs ▪ Fewer safety regulations ▪ Effective against Cryptosporidium ▪ Provides better taste and odour control than chlorination	▪ More complicated than chlorine or UV systems ▪ No residual protection for drinking water ▪ Hazardous gas requires special handling By-product formation ▪ Generally higher cost than chlorine	Bromoform, MBAA, DBAA, bromides, carboxylic acids, aldehydres, ketones, ketoacids.
UV	▪ No chemical generation, storage, or handling ▪ Effective against Cryptosporidium	▪ No residual protection ▪ Less effective in turbid water ▪ No taste and odour control ▪ Generally higher cost than chlorine	No known by-products at levels of concern.
Chlorine dioxide	▪ Effective against Cryptosporidium ▪ No formation of THMs, HAAs ▪ Provides better taste and odours control than chlorination	▪ By-product formation ▪ Requires on-site generation equipment and handling of chemicals ▪ Generally higher cost than chlorine	Chlorites, chlorates.

Table A.7: A detailed summary of the methods used for the analyses of THMs reported in literature.

Technique	Further information	Instrumental analysis time	Linear range (Correlation coefficient (R^2))	Repeatability RSD % (Conc and n)	Limit of detection (µg/l) (recovery, where reported, %)	Reference
HS-GC-MS	Static HS	< 16 min	0.01 - 50 µg/l	4.2 - 5.8 % (0.2 µg/l, n=11)	0.003 - 0.01 µg/l	(Caro *et al.*, 2007),
HS-GC-MS	Static HS	n/k	n/k	n/k	0.2 - 0.3 µg/l (94 - 114 %	(Duong *et al.*, 2003)
HS-GC-MS	n/k	< 6 min	0 - 80 µg/l (0.970 – 0.990)	< 32.8 % (40 and 60 µg/l, n=3)	< 0.1 µg/l	(Culea *et al.*, 2006)
HS-GC-MS	Static HS	n/k	n/k	9.7 - 14.2 % (10 µg/l , n=5)	0.05 - 0.2 µg/l (112 - 123 %)	(Nikolaou *et al.*, 2002b)
HS-GC-MS	Static HS 34 other VOCs	< 20 min	n/k	9.5 - 23.4 % (2 µg/l, n=5)	0.1 µg/l (79 - 89 %)	(Golfinopoulos *et al.*, 2001)
HS-GC-ELCD	Static HS	< 20 min	n/k	1.5 - 10.9 % (15 µg/l, n=6)	0.34 - 1 µg/l (96 - 99 %)	(Badawy, 1992)

Technique	Further information	Instrumental analysis time	Linear range (Correlation coefficient (R^2))	Repeatability RSD % (Conc and n)	Limit of detection (µg/l) (recovery, where reported, %)	Reference
HS-GC-ECD	Static HS	< 20 min	0.1 - 75 µg/l (0.996 - 0.999)	0.6 - 3.3 % (50 µg/l, n=6)	0.1 - 0.2 µg/l (98 - 110 %)	(Kuivinen *et al.*, 1999)
HS-GC-ECD	Static HS	< 20 min	1 - 100 µg/l (0.9936 - 0.9989)	1.3 - 3.0 % (20 & 80 µg/l, n=10)	0.2 - 0.6 µg/l (93 - 120 %)	(Ristoiu *et al.*, 2009)
HS-GC-ECD	Only $CHCl_3$ and $CHCl_2Br$ Static HS	n/k	n/k	n/k	3 µg/l (94 - 99%)	(Toussaint *et al.*, 2001)
HS-GC-ECD	Dynamic HS	< 20 min	0.1 - 200 µg/l (n/k)	2.4 - 9.4 % (n/k)	0.01 - 0.1 µg/l (85 - 148 %)	(Wang *et al.*, 1995)
HS-SPME-GC-MS	PDMS fibre	< 15 min	10 - 160 µg/l (0.9920 - 0.9959)	0.9 - 19 % (n=7)	1.0 - 2.8 µg/l	(Stack *et al.*, 2000)
HS-SPME-GC-MS	CAR PDMS fibre	< 8 min	0.2 - 48 µg/l (0.990-0.998)	6.4 - 15.5 %	0.078 - 0.52 µg/l	(SanJuan *et al.*, 2007)
HS-SPME-GC-MS	PDMS DVB fibre	< 8 min	0.05 - 150 µg/l (0.9990 - 0.9999)	0.56 - 3.75 %	0.001 - 0.006 µg/l (96 -101 %)	(SanJuan *et al.*, 2007)
HS-SPME-GC-MS	n/k	< 11 min	0.05 - 80 µg/l (0.9976 - 0.9998)	0.8 - 2.9 % (40 µg/l, n=5)	0.005 - 0.001 µg/l	(Cho *et al.*, 2003)

Technique	Further information	Instrumental analysis time	Linear range (Correlation coefficient (R^2))	Repeatability RSD % (Conc and n)	Limit of detection (µg/l) (recovery, where reported, %)	Reference
HS-LPME-GC-MS	15 ml HS in 40 ml vial. 10 min extraction @ 20 °C	< 15 min	1 - 100 µg/l (0.9980 - 0.9992)	n/k	0.15 - 0.40 µg/l (101 - 112 %)	(Zhao *et al.*, 2004)
DAI-GC-ECD	n/k	n/k	n/k	2.7 - 15.9 % (30 µg/l, n=6)	3 - 5 µg/l (99 -109 %)	(Golfinopoulos *et al.*, 2001)
LLE-GC-MS	MTBE extraction	n/k	0 - 80 µg/l 0.960 - 0.991	13.6 - 26.4 % (40 µg/l, n=	0.02 - 0.2 µg/l	(Culea *et al.*, 2006)
LLE-GC-ECD	60 other DPBs analysed.	< 25 min THMs	n/k	2.8 - 4.1% (5 , n=8)	0.008 - 0.08 (98 - 101 %)	USEPA Method 551.1, 1995)
LLE-GC-ECD	18 other DPBs analysed.	< 25 min (THMs)	n/k	0.7 - 2.7 % (0.2 - 2.0, n=7)	0.002 - 0.012 (80 – 109 %)	USEPA Method 551, 1990)
LLE-GC-ECD	13 other VOCs	n/k	n/k	0.9 - 2.4 % (10 µg/l, n=5)	0.005 - 0.01 µg/l (90 - 94.7 %)	(Nikolaou *et al.*, 2002b)
LLE-GC-ECD	Hexane extraction	< 10 min	n/k	1 - 2 % (2 µg/l, n=6)	0.8 - 1.0 µg/l (101 -104 %)	(Golfinopoulos *et al.*, 2001)
LLE-GC-MS	Pentane extraction	< 6 min	n/k	n/k	0.03 - 0.05 µg/l	(Yu *et al.*, 1999)

Technique	Further information	Instrumental analysis time	Linear range (Correlation coefficient (R^2))	Repeatability RSD % (Conc and n)	Limit of detection (µg/l) (recovery, where reported, %)	Reference
LLE-GC-MS	13 other VOCs	< 35 min	n/k	4.1 - 4.9 % (10 µg/l, n=5)	0.01 - 0.03 µg/l (127.6 - 138.4 %)	(Nikolaou *et al.*, 2002b)
PT-GC-ECD	Charcoal and Vocarb 3000 trap	n/k	n/k	3.7 - 19.3 % (2 µg/l, n=6)	0.03 - 0.05 µg/l (101 - 124 %)	(Golfinopoulos *et al.*, 2001)
PT- GC-MS	Charcoal and Vocarb 3000 trap (41 VOC)	n/k	n/k	6.5 - 20.6 % (10 µg/l, n=6)	0.25 - 0.1 µg/l (77 - 88 %)	(Golfinopoulos *et al.*, 2001)
PT-GC-MS	Charcoal trap	n/k	0 - 80 µg/l (0.840 - 0.930)	2.3 - 30.4 % (20 µg/l, n=5)	< 1 µg/l	(Culea *et al.*, 2006)
PT-GC-MS	13 other VOCs Vocarb 3000 trap	n/k	n/k	3.7 - 4.9 % (10 µg/l, n=5)	0.01 - 0.05 µg/l (89 - 99 %)	(Nikolaou *et al.*, 2002b)
PT-GC-MS	$CHCl_3$ only (27 VOC)	< 10 min	n/k	54 % (50 µg/l, n=10)	0.02 µg/l (91.6 %)	(Huybrechts *et al.*, 2000)
PT-GC-MS	Chromatography column trap	< 20 min	n/k	0.05 - 1.4 % (1.2 - 23 µg/l, n=8-12)	n/k (88 - 100 %)	(USEPA Method 501.1, 1979a)
PT-GC-MS	84 other compounds	< 20 min (THMs)	n/k	6.1 - 6.4 % (0.1 µg/l, n=7)	0.03 - 0.12 µg/l (90 - 101 %)	(USEPA Method 524.2, 1995c)

Technique	Further information	Instrumental analysis time	Linear range (Correlation coefficient (R^2))	Repeatability RSD % (Conc and n)	Limit of detection (µg/l) (recovery, where reported, %)	Reference
PT- GC-ELCD	VOC (80 others)	< 60 min	n/k	2.5 - 5.2 (10 µg/l, n=7)	0.02 - 1.6 µg/l (98 - 106 %)	(USEPA Method 502.2, 1995)
PT-GC-DELCD	n/a	< 11 min	0.3 - 50 µg/l (0.994 - 0.998)	1.2 - 2.8 % (2 - 48 µg/l, n=7)	0.1 - 0.8 µg/l (110 - 128 %)	(Brown *et al.*, 2007)
CMS-GC-ECD	n/a	< 4 min	0.9 - 35 µg/l (0.987 - 0.997)	4.3 - 8.6 % (1 - 20 µg/l, n=7)	0.1 - 0.4 µg/l (100 - 125 %)	(Brown *et al.*, 2006)
CMS-FIA NCA-FL	n/a	n/k	10 - 100 µg/l (0.976 – 0.989)	2.9 - 14 %	2.1 - 9.4 µg/l (110 - 143 %)	(Geme *et al.*, 2005)
MIMS	n/a	< 6 min	n/k (< 0.9999)	n/k	0.025 - 0.2 µg/l	(Bauer *et al.*, 1994)

n/k - not know, data not available, n/a - not available.

CAR - carboxen
CMS - capillary membrane sampling
DELCD - dry electrolytic conductivity detector
DVB - divinylbenzene
ELCD - electrolytic conductivity detector
MIMS - membrane introduction mass spectrometry
MTBE - methyl tert-butyl ether
PDMS - polydimethylsiloxane
CMS-FIA NCA-FL - capillary membrane sampling-flow injection analysis method with nicotinamide fluorescence
PID - photoionisation detector
VOC - volatile organic compounds

Table A.8: A detailed summary of the methods utilised for the analyses of HAAs reported in literature.

Measuring device	Sample Preparation	Instrumental analysis time (min)	Linear range and correlation coefficient (R^2)	Limit of detection (µg/l) (recovery, where applicable, %)	HAAs detected	Reference Location, if reported
LLE-GC-µECD	*Extensive preparation* Derivatisation (extraction + methylation) US EPA methods	> 55 min	n/k	0.6 - 1.3 µg/l	HAA6	(Rodriguez *et al.*, 2007) Canada
			n/k	0.07 - 0.82 µg/l	HAA9	(USEPA 552.2, 1995)
			1 - 20	0.012 - 0.17 µg/l (98.2 - 111 %, 10 µg/l)	HAA9	(USEPA 552.3, 2003)
			n/k	0.4 - 1.3 µg/l	HAA6 (BDCAA instead of MCAA)	(Malliarou *et al.*, 2005) Europe
			n/k	0.6 - 1.3 µg/l	HAA6	(Rodriguez *et al.*, 2004) Canada
			n/k	0.066 - 0.82 µg/l	MBAA, DCAA, TCAA, DBAA, TBAA	(Marhaba and Van, 2000) USA
			n/k	n/k (52 - 105 %)	HAA9	(Pourmoghaddas *et al.*, 1993) USA

Measuring device	Sample Preparation	Instrumental analysis time (min)	Linear range and correlation coefficient (R^2)	Limit of detection (µg/l) (recovery, where applicable, %)	HAAs detected	Reference Location, if reported
LLE-GC-ECD	*Extensive preparation* Derivatisation (extraction + methylation (non-EPA)	< 35 min	0.5 - 30 >0.99	0.37 -23.6 µg/l (78.1 -123.7 %)	HAA9	(Nikolaou *et al.*, 2002a) Greece
LLE-GC-ECD	*Extensive preparation* Derivatisation (extraction + diflouroanilide)	n/k	n/k	0.6 - 2 µg/l	MCAA, DCAA, TCAA	(Ozawa *et al.*, 1990) Japan
SPME-GC-ECD	*Extensive preparation* Derivatisation (LLME + methylation)	< 7 min	n/k	0.6 -7.2 µg/l	HAA9	(Wu *et al.*, 2002) Canada
HS-SPME GC-MS	*Extensive preparation* Derivatisation (extraction + ethylation)	< 35 min	0.5 - 135 (0.998 - 0.999)	0.01 - 0.20 µg/l	HAA6	(Sarrión *et al.*, 1999) Spain
HS-LPME-GC-MS	*Extensive preparation* Derivatisation	> 22 min	0.5 - 300	0.02 - 0.4 µg/l (94 - 99 %)	HAA9	(Cardador *et al.*, 2008)
LLE GC-MS	*Extensive preparation* Derivatisation (extraction + methylation) US EPA methods	< 55 min	n/k	0.07 - 0.83 µg/l (73 -165 %)	HAA9	(Xie, 2001) USA
			n/k	0.001 - 0.05 µg/l	MCAA, MBAA, DCAA, DBAA	(Scott *et al.*, 1998) Canada

Measuring device	Sample Preparation	Instrumental analysis time (min)	Linear range and correlation coefficient (R^2)	Limit of detection (µg/l) (recovery, where applicable, %)	HAAs detected	Reference Location, if reported
SPE-HPLC-EC	*Moderate preparation* Direct evaporation and solid phase extraction (SPE)	< 30 min	n/k	120 - 10,000 µg/l	HAA6 (TBAA instead of DBAA)	(Carrero *et al.*, 1999) USA
HPLC	*Moderate preparation*	< 10 min	n/k	30 - 40 µg/l	DCAA, DBAA, TCAA, TBAA	(Heller-Grossman *et al.*, 1993) Israel
HPLC-UV	*Minimal preparation*	n/k	n/k	0.02 - 2.69 µg/l (66.1 - 100.8 %)	HAA6	(Kou *et al.*, 2004)
SDME-GC-MS	*Moderate preparation*	n/k	0.5 - 100 > 0.9915	0.1 - 1.2 µg/l (82.5 - 97.6 %)	HAA6	(Saraji *et al.*, 2009)
IC-ICP-MS	*Minimal preparation*	< 5 min	0.9976 - 0.9993	0.37 - 127.6 µg/l (91.7- 103.8 %)	HAA9	(Liu *et al.*, 2004) China
SPE-CE UV	*Moderate preparation* SPE extraction Filtration through a 0.0.2 µm pore size	< 10 min	40 - 140 0.991 - 0.996	n/k	HAA5	(Martínez *et al.*, 1999) Spain
CE UV	*Moderate preparation* Filtration through a 0.45 µm pore size filter capsule	< 10 min	n/k	683 - 1507 µg/l	TCAA, CDBAA, BDCAA, TBAA	(Hozalski *et al.*, 2001) USA

Measuring device	Sample Preparation	Instrumental analysis time (min)	Linear range and correlation coefficient (R^2)	Limit of detection (µg/l) (recovery, where applicable, %)	HAAs detected	Reference Location, if reported
			n/k	140 - 1062 µg/l	MCAA, MBAA, TCAA	(McRae *et al.*, 2004) USA
SPE IC	*Minimal preparation*	n/k	0.979 -0.999	19 - 130 µg/l	MCAA, MBAA, DCAA, TCAA, DBAA	(Barron *et al.*, 2004) Ireland
SPE-LC-ESI-MS	*Moderate preparation* SPE extraction	< 20 min	0.9991 - 0.9995	0.024 - 0.118 µg/l	HAA9	(Takino *et al.*, 2000)
ESI-FAIMS-MS	*Minimal preparation*	n/k	0.9965 - 0.9996	0.5 - 4 µg/l	n/k	(Ells *et al.*, 2000) Canada
		n/k	n/k	0.05 - 0.31 µg/l	HAA6 (and BDCAA)	(Gabryelski *et al.*, 2003) Canada
CMS-FIA NCA-FL	*Minimal preparation*	< 40 min	0.978 - 0.997	2.0 - 5.9 µg/l	HAA5	(Geme *et al.*, 2005)
CE-ESI-MS	*Minimal preparation* Extraction	< 10 min	n/k	~ 0.07 µg/l	n/k	(Urbansky, 2000) USA

n/k – not known, data not available.

CE-UV - capillary electrophoresis (CE) with UV detection,
FAIMS-ESI-MS - high-field asymmetric waveform ion mobility spectrometry - electrospay ionisation - mass spectrometry,
HPLC-EC - high pressure liquid chromatography-electrochemical detection,
HS-LPME-GC-MS- headspace-liquid phase micro extraction gas chromatography mass spectrometry,
IC-MS - ion chromatography-mass spectrometry,
ICP-IC-MS - inductive coupled plasma -ion chromatography-mass spectrometry,
SPE-IC - solid phase extraction- ion chromatography.
CMS-FIA NCA-FL - capillary membrane sampling-flow injection analysis method with nicotinamide fluorescence,
SPE-LC-ESI-MS - solid-phase extraction-liquid chromatography electrospray ionisation mass spectrometric detection.

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Appendix 2 - Liquid Liquid Extraction method details for THMs

The method for the preparation of the THMs using the LLE method.

This was the procedure used by members of Cranfield Water Science Institute for the sample preparation of THMs through LLE method, according to the USEPA Method 551.

A 50 ml of the water sample was collected, buffered at pH 4.5 - 5.5 (1 % w/w Na_2HPO_4 and 99% KH_2PO_4) and quenched with sodium sulphite solution. The extraction was carried out with methyl tert-butyl ether (MTBE) containing the internal standard (bromofluorobenzene, 1000 µg/l). After addition of the surrogate (Section 11.1.3) transfer 3.0 ml of MTBE by an automatic dispensing pipette together with 20 g Na_2SO_4 to the sample vial. Recap and extract the NaCl or Na_2SO_4/MTBE/sample mixture by vigorously and consistently shaking the vial by hand for four minutes. Invert the vial and allow the water and MTBE phases to separate. Transfer a portion of the solvent phase from the 60 ml vial to an autosampler vial

Appendix 3 - Further details on the formation potential experiments of THMs and HAAs

A) The schematic of the two water sources

This section describes sources of the two water treatment works (WTW) from which the samples were taken for the study reported in Chapter 6. The two water sources were selected based on the type and nature of the water sources. The Grafham WTW was chosen as it had a high bromide content, while Albert WTW was chosen as an upland water, which contained less bromide and less alkalinity. The schematics of the two water sources are shows by the Figures below. The sampling points at each works are denoted by ^{x}.

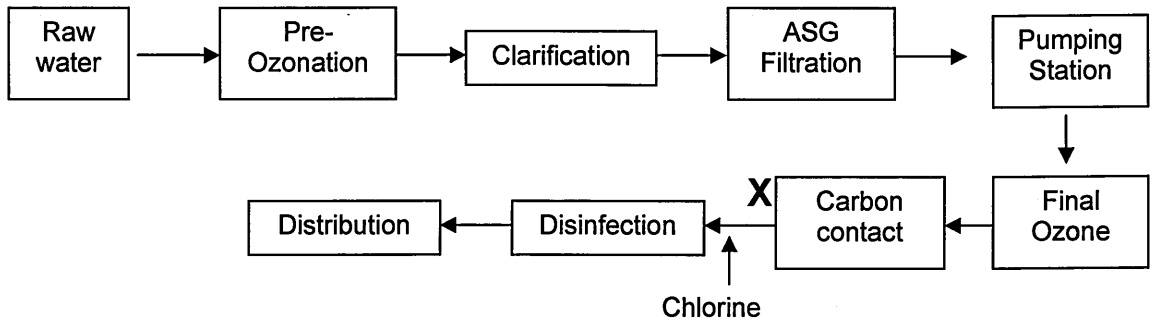

Figure A.1: The process schematic for lowland water source (Anglian Water)

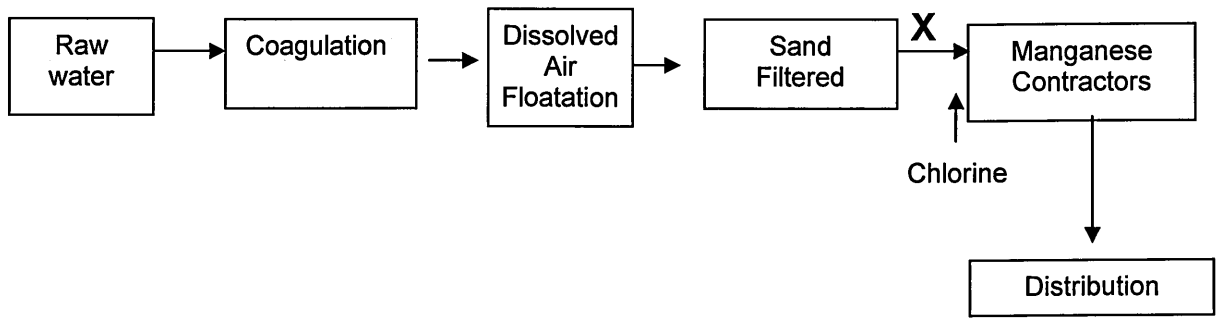

Figure A.2: The process schematic for upland water source (Yorkshire Water Services Ltd)

B) Preparation of hypochlorite solution

The determination of strength of hypochlorite (HOCl) solution – sodium hypochlorite (8 %), 3 ml solution was diluted to 600 ml in a glass bottle with reverse osmosis (RO) water and mixed well. The diluted solution (100 ml) was placed in a conical flask containing 5 ml acetic acid glacial and 1 g potassium iodide. The contents of the flask were mixed and titrated with standard 0.1M sodium thiosulphate until the yellow colour of the liberated iodine was almost discharged. Approximately 1 ml of starch solution (5 g/l) was added and the titration continued until a blue/black colour was observed. The volume was recorded. The chlorine concentration of the sodium hypochlorite was then calculated using the following equation:

$$Hypochlorite\ concentration\ (mg/l\ Cl_2) = \frac{(M \times 35450 \times titrant\ volume\ (ml))}{hypochlorite\ added\ (ml)}$$

M is the molarity of the sodium thiosulphate
35450 is a coeffication of

The strength of the hypochlorite solution was measured every week. The sodium hypochlorite solution was discarded when the concentration fell below 20 mg Cl_2 /l (every two weeks).

C) Preparation of phosphate buffers

The stock solutions of sodium phosphate dibasic (Na_2HPO_4) at 1/15 M and potassium acid phosphate (KH_2PO_4) at 1/15 M were prepared respectively by dissolving 4.733g in 0.5 l of ultrapure water and 4.540 g in 0.5 l of ultrapure water. The buffer at pH 6 was made up by adding 88 ml of the KH_2PO_4 stock solution to 12 ml of Na_2HPO_4. Buffer at pH 7 was made up by adding 27 ml of the KH_2PO_4 stock solution to 73 ml of Na_2HPO_4. The buffer at pH 8 was made up by adding 4 ml of the KH_2PO_4 stock solution to 96 ml of Na_2HPO_4. Buffer was made fresh when the pH fell below 0.2 pH unit of the expected value.

D) Preparation of sodium sulphite solution

The sodium sulphite (10 g) was dissolved in 100 ml ultrapure water. The solution was used for dechlorination, and was discarded after 2 weeks. A volume (0.1 ml) destroyed about 5 mg residual chlorine.

E) Determination of the chlorine residual

Determination of the chlorine residual was carried out using an adaptation of procedure 4500-Cl in 'Standard Methods for the Examination of Water and Wastewater' (American Public Health Association 1992) and is described below. After the bottles were stored for the contact time required, the chlorine residual was measured as follows:
Titration is carried out away from direct sunlight. The burette is filled up with 0.01 N of thiosulphate ($Na_2S_2O_3$). In a conical flask, 5 ml of acetic acid and about 1g of potassium iodide (KI) are placed. Then a volume sample of 100 ml is added. Titration is carried out until the end point is reached until the yellow colour of the liberated iodine is almost discharged. Starch solution is added and titrated until blue colour is discharged.

Blank titration: This is carried out to correct the result of sample titration by determining the blank contribution by oxidizing or reducing reagent impurities. The blank also compensates for the concentration of iodine bound to starch at the end point. A volume of RO water corresponding to the volume sample used for titration is placed in a conical flask followed by 5 ml of acetic acid, plus 1 g of KI. The titration is performed as below.
Before calculating the chlorine concentration, the blank titration is subtracted from the sample titration; or, if necessary, the net equivalent value is added to the blank titration.
The chlorine residual was calculating using Equation 4

$$\textit{Chlorine Residual (mg Cl as } Cl_2/l) = Co - \frac{(A \pm B) \times N \times 35450}{D}$$

Co = concentration initial chlorine dose (mg Cl as Cl_2/l)
A = ml titration for sample,
B = ml titration for blank (positive or negative)
N = normality of $Na_2S_2O_3$
D = normality of $Na_2S_2O_3$

F) Schematic of HAA sample preparation

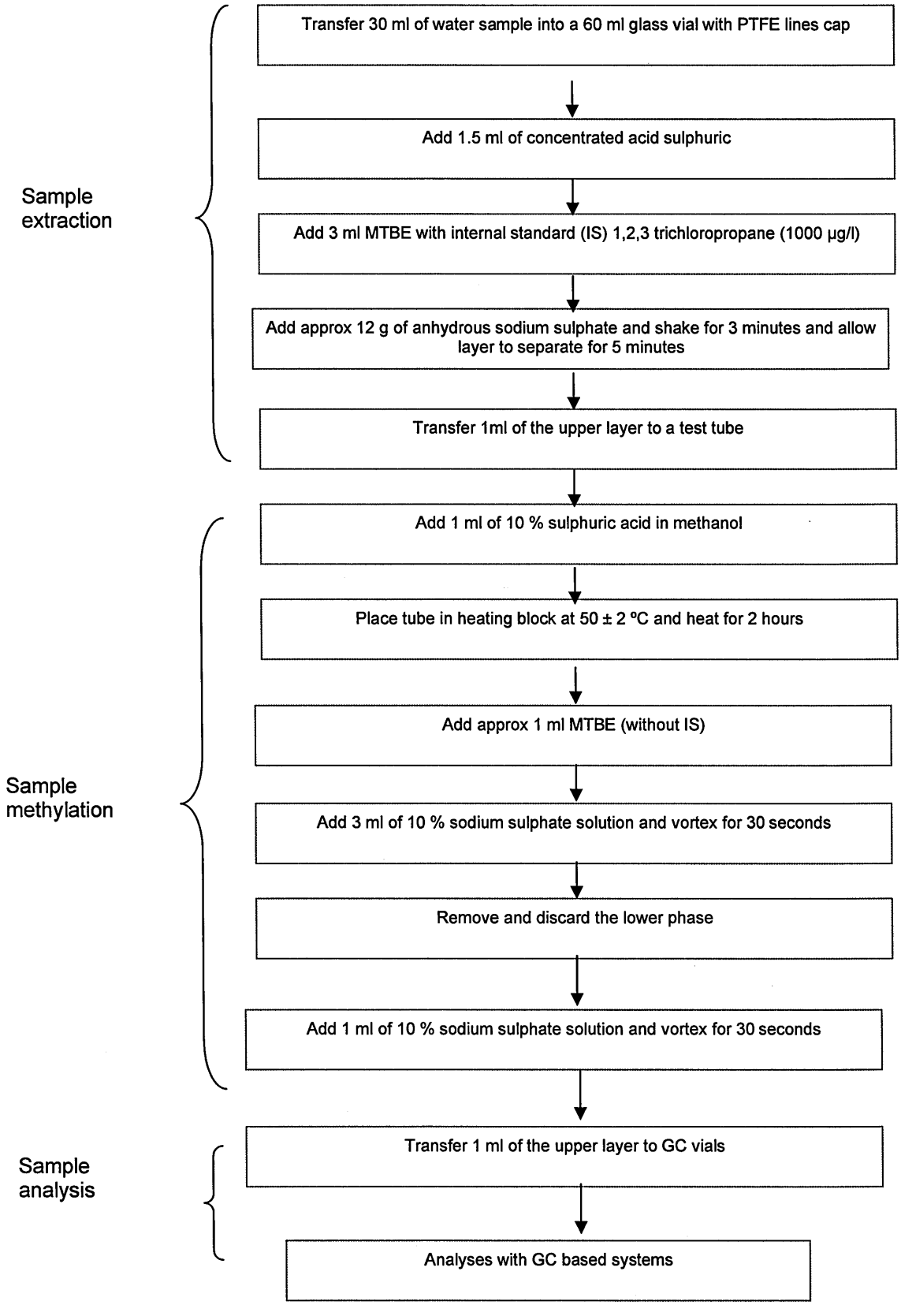

Figure A.3: Schematic of the HAA derivatisation procedure used by Cranfield University, which is a modified version of USEPA Method 552.2 and is reported by Tung et al., (2006).

Appendix 4 - Published Chapter

The preliminary findings of Chapter 6 of this thesis were published jointly as Chapter 7 of the book, "*Disinfection By-Products in drinking Water: Occurrence, Formation, Health Effects, and Control*" from American Chemical Society Symposium Series 995 (.

This study was performed collaboratively by members of Cranfield University and The Open University. The sampling, sample preparation and sample derivatisation were performed at Cranfield University, whilst all the instrument optimisations, sample analyses and concentration determinations were conducted by the author at The Open University with the support of his supervisors.

Parameters affecting Haloacetic Acid and Trihalomethane Concentration in UK Drinking Water

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Parameters affecting the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) were investigated by chlorinating two geographically different waters in the UK: lowland and upland water. Parameters were pH, bromide addition and temperature. The greatest impact of pH was observed in the formation of THMs in the lowland water. The structure of the precursors was found to be more important when determining HAA formation than the chlorination pH. Addition of bromide had a greater impact in the upland water.

Reducing the temperature from 20°C to 7°C resulted in a mean decrease of DBP concentration by 50%. The difference in natural organic matter (NOM) structure was believed to account for such differences in the final results.

Natural organic matter (NOM) is described as an intricate mixture of organic compounds that occurs universally in ground and surface waters. Whilst NOM itself is not problematic, it can be converted to disinfection by-products (DBPs) when chlorine is used during water treatment (*1*). In the UK, regulated disinfection by-products (DBPs) include trihalomethanes (THMs). These are regulated at 100 µg/L in a single sample (*2*). Recently it has been observed that THMs may not be the major representative of the chlorinated DBPs. For instance, in the US, levels of haloacetic acids (HAAs) have been reported at similar or higher levels than THMs in finished drinking waters (*3*).

In the US, four THMs and five of the HAAs are regulated at values of 80 µg/L and 60 µg/L respectively (*4*). In the future, HAAs may be regulated in Europe (*5*). Currently HAAs are not routinely measured in the UK and very little is known about the formation of HAAs in UK waters. To our knowledge, only one UK study has been published that reports HAA levels up to 244 µg/L (*6*).

The formation of HAAs is influenced by a number of factors. These include the disinfection parameters such as the disinfectant used, its concentration, the contact time, water temperature and water pH. HAA formation will also be affected by the quality of the water being subjected to disinfection. The type and concentration of natural organic matter (NOM) and the concentration of bromide will directly impact on the level of HAAs formed (*7, 8*).

In the case of chlorine, generally the longer the contact time and the higher the concentration, the more DBPs will be formed (*9*). It is known that the formation of THMs is enhanced at high pH (*10*). However, the effect of pH on the formation of HAAs is equivocal. Overall, HAA formation increases with decreasing pH. However, the concentrations of dichloroacetic acid and trichloroacetic acid have been found to decrease with decreasing pH (*11*). High NOM concentrations have generally been associated with high DBP concentrations (*12, 13, 14*). In the UK, chlorination tends to occur after the water has been treated by a coagulant and filtered (*15, 16*). Here, the NOM is mainly hydrophilic in character and low in concentration (*17*). However, hydrophilic NOM has been reported to contribute substantially to the formation of DBPs especially for

waters with a low humic (hydrophobic) content (*7*). The presence of bromide in water will influence the speciation of the DBPs and the amount of bromine present will also affect the concentration of the DBPs. Waters with levels of bromide as low as 100 µg/L have been reported to form brominated HAAs and THMs (*8*). It should also be remembered that precursor removal by coagulation will increase the ratio of bromide to DOC and may result in increased formation of brominated DBP species (*18*).

HAAs are highly water-soluble DBPs that exist as ions at ambient pH. For analysis by gas chromatography (GC), they must first be converted to their protonated forms before extraction from water with organic solvent and then derived to form more volatile methyl esters (*19*). As HAAs exist as ions, it is possible to analyse them directly using ion chromatography (IC) (*20*) or capillary electrophoresis (CE) (*21*) but only at higher levels than with GC coupled with electron capture detector (ECD). In this study, GC with mass spectrometer (GC-MS) and GC-ECD were investigated as analysis techniques.

This study reports the concentration of THMs and HAAs when two distinctly different waters are chlorinated under controlled conditions. The study also investigates the impact of pH, temperature and bromide content on the formation of THMs and HAAs. The waters are from different geographical regions. They were collected after treatment by coagulation but before disinfection. Thus we have two waters that have been treated to remove hydrophobic organic material, and have low SUVA values. The aim of this work was to determine the sensitivity of DBP formation to differences in water character.

Material and Methods

Water Samples and Characterisation

All experiments were undertaken with water collected from two water utilities: Anglian Water from East Anglia (lowland water) and Yorkshire Water (upland water). The lowland water was pre-ozonated, coagulated, sand filtered and was collected after contact with granular activated carbon. The upland water was coagulated and was collected after sand filtration. On collection, the waters had not been in contact with disinfectant. The water treatment works (WTWs) were selected because of their different organic matter content as well as their different geographical position. A large volume of each water was collected (≥100 L) and stored at 5°C until used. To ensure consistency, periodic measurements of pH, non purgeable organic carbon (NPOC), ultraviolet absorbance at a wavelength of 254 nm (UV_{254}) and bromide concentration were carried out.

NPOC was measured using a Shimadzu TOC-5000A analyser (Shimadzu, Milton Keynes, UK). Samples were acidified and purged to convert the inorganic carbon to CO_2. UV_{254} was measured using a Jenway 6505 UV/VIS spectrophotometer (Patterson Scientific Ltd., Luton, UK). Analysis of bromide was carried out with an ion chromatography (IC) system, (Dionex DX500 series, Dionex, UK).

Fractionation

To determine the hydrophilic/hydrophobic ratio, 50 litres of the treated waters were fractionated by XAD and cation exchange resin adsorption techniques into their hydrophobic neutral (HPO-N), hydrophobic acid (HPO-A), transphilic dissolved organic matter (TPI-DOM), hydrophilic base (HPI-B) and hydrophilic acid + neutral (HPI-A+N) fractions. The method used was adapted from Leenheer et al. (*22*).

The resins used were Amberlite XAD-7HP resin and Amberlite XAD-4 resin (Rohm & Haas, Germany). Amberlite XAD-7HP is an acrylic ester polymer and is equivalent to XAD-8; Amberlite XAD-4 is a styrene divinylbenzene polymer. Amberlite 200 strongly acidic cation exchanger has a sulfonated polystyrene/DVB matrix (Sigma-Aldrich, UK). The XAD resins were prepared by sequentially Soxhlet extracting for 48 hours each with methanol, acetonitrile and methanol again to remove impurities. Before use the resins were packed into columns and rinsed with deionised water (DI) until the column effluent DOC was < 2 mg/L (*23*).

Chlorination and Kinetic Experiments

The treated waters were chlorinated at pH 6, 7 and 8 to determine their disinfection by-product formation potential (DBP-FP). In addition one set of samples for each water was chlorinated at pH 7 with addition of bromide (200 µg/L) and another set at pH 7 with a temperature of 7°C. Hypochlorite solution was standardised using the 4500-Cl B. Iodometric method I in "Standard Methods for the Examination of Water and Wastewater" (*24*). The chlorine dose required was determined by preliminary chlorine demand experiments such that the free chlorine residual was ≥ 1 mg/L as Cl_2 after seven days of contact time. Before incubation the water to be tested was brought to room temperature and the pH was adjusted using phosphate buffer. A 100 mL bottle was part filled with the water sample, the buffer and the chlorine solution were added and the bottle was filled up and capped headspace free with a PTFE-lined cap. Samples were incubated for 168 hours at 20°C in the dark with the exception of the samples incubated at 7°C.

At the end of the incubation period the chlorine residual was measured using Iodometric method I and an appropriate amount of sulphur-reducing agent (sodium sulphite) was added to the samples to destroy the chlorine residual whilst not degrading HAAs (*19*).

For the measurement of THMs, 5 mL of water sample was pipetted into a 10 mL vial to allow 5 mL of headspace. Samples were prepared in duplicate and analysed in triplicate.

HAA samples were first converted to their protonated forms before processing the extraction with organic solvent and deriving to form methyl esters. The method used for the derivatisation is adapted from USEPA Method 552.3.

Analytical Methods

THMs were analysed using a Varian Saturn 2200 (ion-trap) gas chromatograph-mass spectrometer (GC-MS). The samples were heated and agitated by CTC CombiPal to 60°C for 30 minutes. 500 μL of headspace was removed by heated syringe and injected with a 10:1 split, separation was performed by a BPX5 column (SGE; 30 m × 0.25 mm id × 0.25 μm film thickness) with a helium carrier gas at a column flow rate of 1.1 ml/min. The injector temperature was 250°C; the initial oven temperature was 45°C for 2 minutes followed by a 10°C per minute temperature ramp to 90°C. The MS was operated in the electron ionisation (EI) mode. The ion-trap temperature was set at 230°C and the electron energy was 70 eV. Mass spectra were collected in full scan mode (33-300 amu). The ions of 83, 129 and 173 m/z were selected as quantification ions. Quantification of THMs was achieved by comparing the chromatograms of the samples with the calibration curves from standards.

HAA standards were run with a GC Perkin Elmer AutoSystem XL coupled with a TurboMass Gold MS using the method reported in a study of Xie (*25*).

HAAs were also measured on a gas chromatograph with a micro electron capture detector (Agilent 6890 GC-μECD). A volume of 1 μL was injected with the injector at 200°C with a 5:1 split, separation was performed by a BPX5 column (SGE; 30 m × 0.25 mm id × 0.25 μm thickness) with a helium carrier gas at a column flow rate of 1.1 ml/min. The initial oven temperature was 35°C followed by a 5°C per minute temperature ramp to 220°C and held for 1 minute. The detector temperature was 230°C and the rate of data collection 20 Hz.

HAA samples were run in parallel by comprehensive two dimensional GC-MS utilising a Leco Pegasus VI GC×GC-time of flight mass spectrometer (GC×GC-TOFMS). GC×GC separation was performed using an Agilent 6890 GC with a Leco GC×GC modulator fitted coupled to a Pegasus IV time-of-flight mass spectrometer (LECO Corporation). The GC injector was operated in splitless mode with a column flow rate of 1.0 ml/min and held at 200°C. GC×GC separation utilised a non-polar column and a polar column a BPX5 (SGE; 30 m × 0.25 mm × 0.25 μm) and a BPX50 (SGE; 1.8 m × 0.1 mm × 0.1 μm) respectively. The GC oven temperature was held for 1 minute at 35°C and ramped to 220°C at a rate of 5°C/min and then held for 1 minute, the second column was ramped at 30°C above the first column. Modulation time was 4 seconds. Mass spectra were acquired in electron ionisation mode from 33 to 400 amu with an acquisition rate of 133 spectra per second.

Results and Discussion

Comparison of Analytical Devices for HAA Measurements

Equipment at Cranfield includes a GC-MS (Perkin Elmer Turbomass). This was used to analyse six out of nine HAA standards (monochloroacetic acid MCAA, monobromoacetic acid MBAA, dichloroacetic acid DCAA, trichloroacetic acid TCAA, bromochloroacetic acid BCAA and dibromoacetic acid DBAA) that had been derived to form their methyl esters. A published method was used to set up the GC-MS (*25*). However it was difficult to quantify derived HAA methyl esters using this method. The peaks were not well resolved nor was the S/N ratio sufficient. The GC-MS was run in the selective ion monitoring (m/z 59) mode but this did not significantly improve the sensitivity (Figure 1).

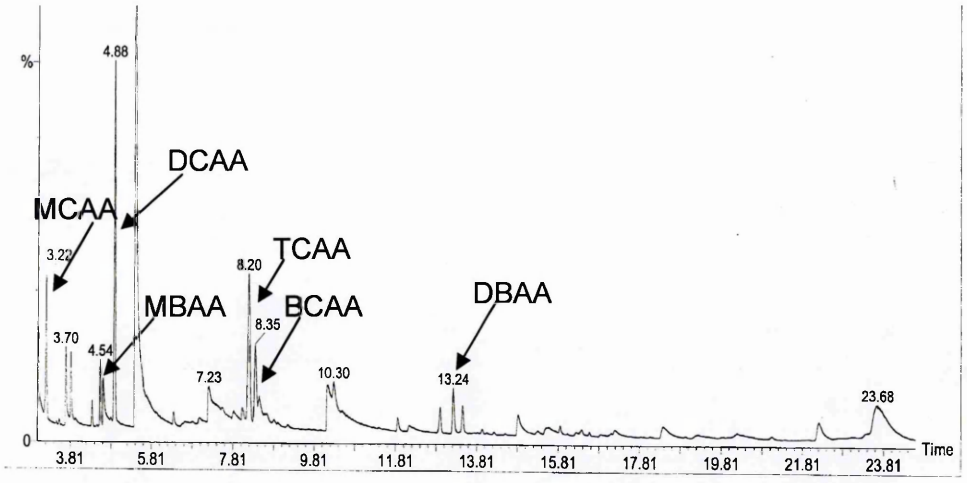

Figure 1. Partial mass chromatogram from Perkin Elmer GC-MS: HAA_6 standard 100 µg/L

In order to confirm the findings, samples were run in parallel using a GC-MS at the Open University (Agilent 5973). The results were comparable.

To investigate the difficulties further, samples were run using a Leco Pegasus 4D GC×GC-TOFMS. This machine uses two GC columns to separate analytes based on volatility as well as polarity. The derived HAA methyl ester peaks could be well observed as they had been separated from the interfering material. The interfering material had a greater intensity than some of the derived methyl esters and also eluted at retention times that overlapped with the derived HAA methyl esters (Figure 2). The interfering peaks are thought to be incurred from the derivatisation procedure.

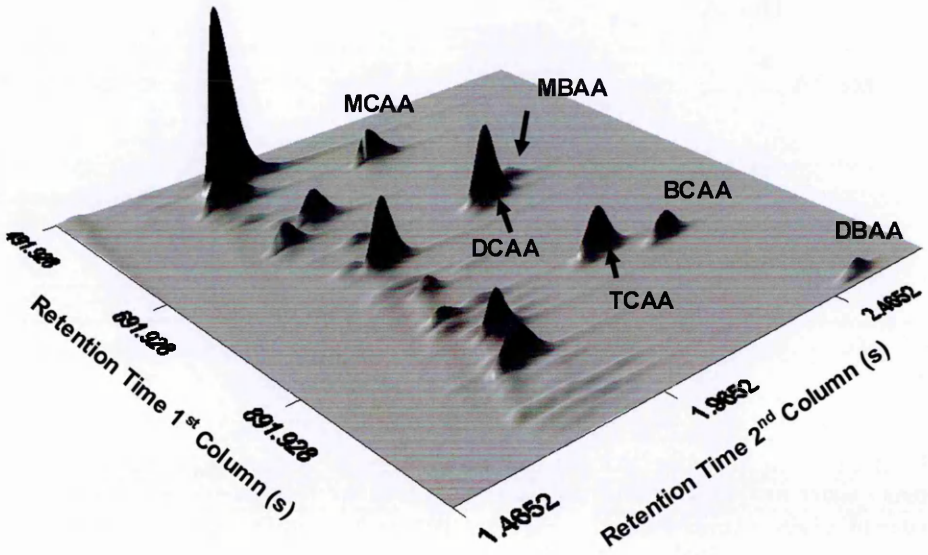

Figure 2. A partially reconstructed mass chromatogram (m/z 59) of a derivatised HAA6 standard (Leco Pegasus 4D GC×GC-TOFMS)

The data produced from the Leco Pegasus 4D GC×GC-TOFMS was used to determine why the GC-MS method was not working. Due to the difficulties encountered using GC-MS, in this study, HAA data collected are based on analysis of samples using GC/ECD (Figure 3 and Figure 4). However, MCAA was not quantified because of results inconsistency and analytical difficulties.

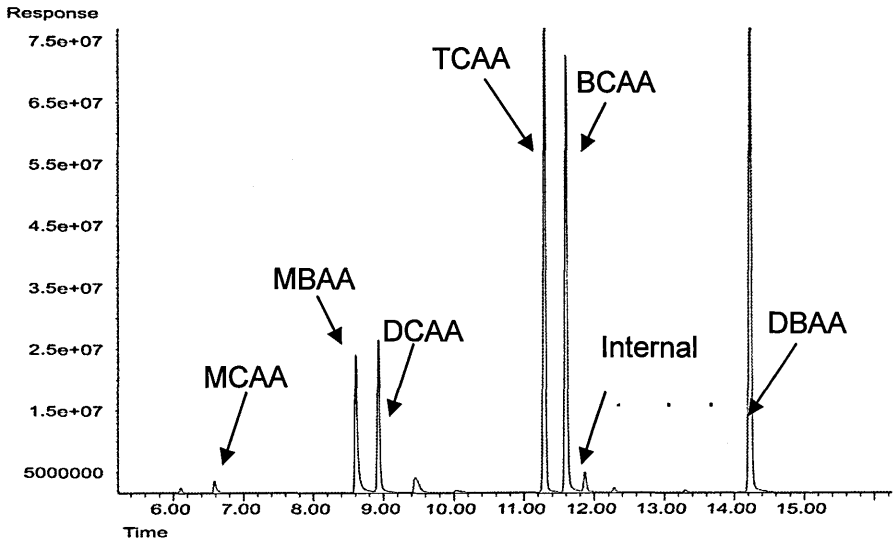

Figure 3. Chromatogram of HAA_6 standard (Agilent 6890 GC-μECD)

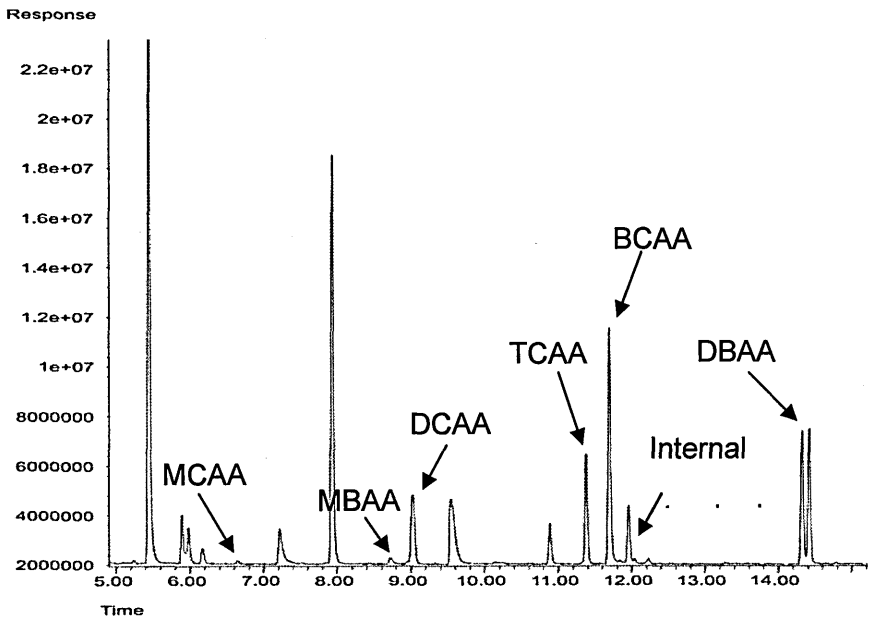

Figure 4. Chromatogram of HAA formed by chlorination of lowland water (Agilent 6890 GC-μECD) – 7 days, pH 7, 20°C

Waters Characterisation

Characteristics of the waters are summarised in Table 1. The concentration of organic matter was greater in the lowland water (4.7 mg/L) than in the upland water (2.1 mg/L). NOM fractionation indicated that organic matter in the upland water had a higher hydrophilic content than the lowland water which had a significant transphilic content (Table 1). Hwang et al. (*26*) reported that the transphilic fraction of intermediate polarity is generally more hydrophobic than hydrophilic but this statement was highly dependent on the water source.

Table 1. Water Characterisation

Parameters	*Upland water*	*Lowland water*
pH	6.7	8.0
NPOC (mg/L)	2.1	4.7
UV_{254} (m^{-1})	4.8	5.9
$SUVA_{254}$ [b] (m^{-1} L mg^{-1} C)	2.3	1.3
Alkalinity (mg/L of $CaCO_3$)	6	188
Bromide content (µg/L)	34	206
THM-FP (pH = 7; temperature = 20°C, µg/L)	72	89
HAA-FP (pH = 7; temperature = 20°C, µg/L)	104	84
Hydrophobic – Neutral (%)	4	2
Hydrophobic – Acid (%)	19	23
Transphilic – Dissolved Organic Matter (%)	8	31
Hydrophilic – Base (%)	2	4
Hydrophilic – Acid + Neutral (%)	67	40

[a] Non purgeable organic carbon
[b] Specific ultraviolet absorbance

The reactivity with respect to DBP formation potential can be characterised with SUVA (*27*). A high SUVA value is an indicator of a high DBP production. Here, the lowland water had a lower SUVA value than the upland water (1.3 and 2.3 respectively), but both waters had a relatively low SUVA given the range (0 – 6) reported by Edzwald and Tobiason (*27*).

As expected, the two waters differed not only in their alkalinity but also in their bromide concentration. The bromide concentration of the lowland water (206 µg/L) is six times higher than that of the upland water (34 µg/L). Thus it is expected that the lowland water will produce more brominated species.

Level of HAAs and THMs measured were similar in the lowland water after 168 hours contact time and at pH 7, whereas the upland water had the potential to form more HAAs. Malliarou et al. (*6*) found that some regions of the UK produced an average total level of THMs higher than the HAAs, while the contrary was found in other regions, which highlights the differences observed in different geographical locations in the UK.

Parameters affecting the Formation of THMs and HAAs

Effect of pH

It is well known that the formation of DBPs is strongly dependant on the chlorination pH (*11*, *28*, *29*).

As shown in Figure 5, increasing pH from 6 to 8 had a slight impact on the formation of HAAs in the lowland water. The HAA formation was 15% less at pH 8 than at pH 6. Liang and Singer (*12*) reported that increasing pH from 6 to 8 had a very little effect on the formation of the monohaloacetic acid (XAA) and dihaloacetic acid (X_2AA) species, but significantly decreased the formation of the trihaloacetic acid (X_3AA) species. Here, DCAA followed by BCAA were found to be more affected by pH than TCAA, but in general the pH had a very little effect on the formation of HAAs with a slight trend of decreasing HAAs with increasing pH. In the literature, DCAA formation was reported to be slightly higher at pH 7 (*11*). This is true of the results found here.

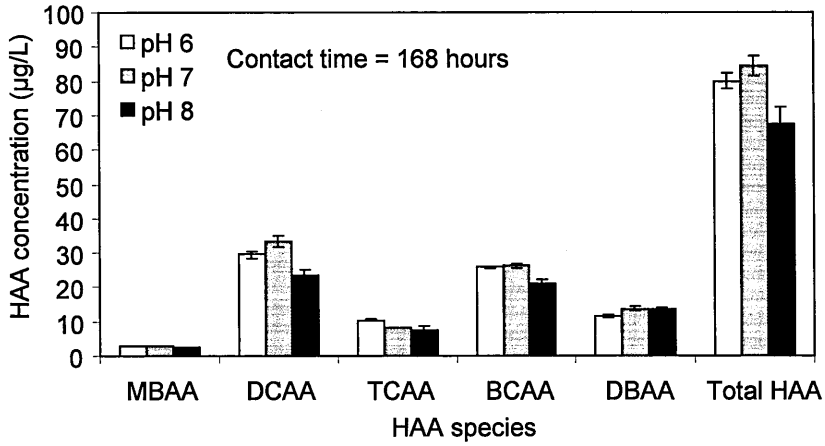

Figure 5. Comparison of pH effect on the formation of measured HAAs in the lowland water

The impact of the pH in the upland water is shown (Figure 6). Formation of HAAs was 14% greater when increasing the pH from 6 to 8 and the lowest concentration was found at pH 7. In the upland water, only TCAA, DCAA and BCAA were detected due to the low bromide content in this water. The DCAA concentration was higher at pH 6 and similar at pH 7 and 8. TCAA increased by 28% with increasing pH, which is contrary to the literature (*30*, *12*) and the results found for the lowland water.

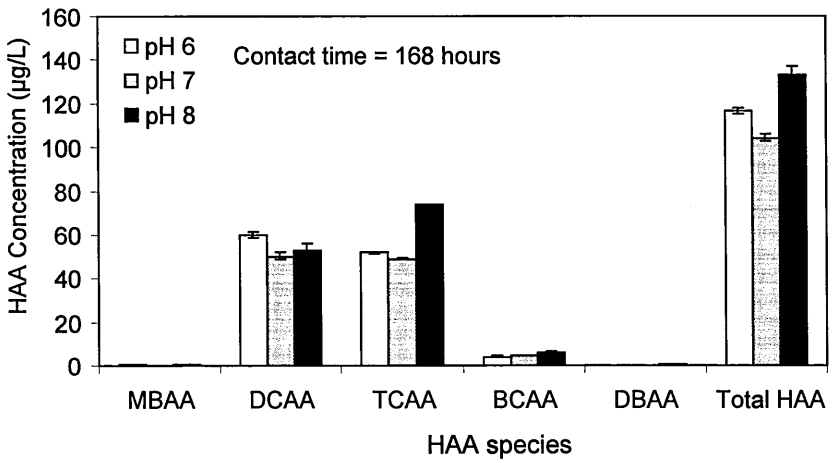

Figure 6. Comparison of pH effect on the formation of measured HAAs in the upland water

The behaviour of DCAA and TCAA is different for the lowland and upland water when changing the pH of chlorination. The lowland water agrees with reported literature (*12*) but the upland water does not follow the same pattern. Precursors are expected to be different which could account for these observations. It can be concluded that the structure of the precursors is more important when determining DCAA and TCAA formation than the chlorination pH.

The impact of pH on the formation of THMs has been widely studied (*31*, *32*, *28*, *29*) and the trend of THMs increasing with increasing pH agrees with the results shown here (Figures 7 and 8).

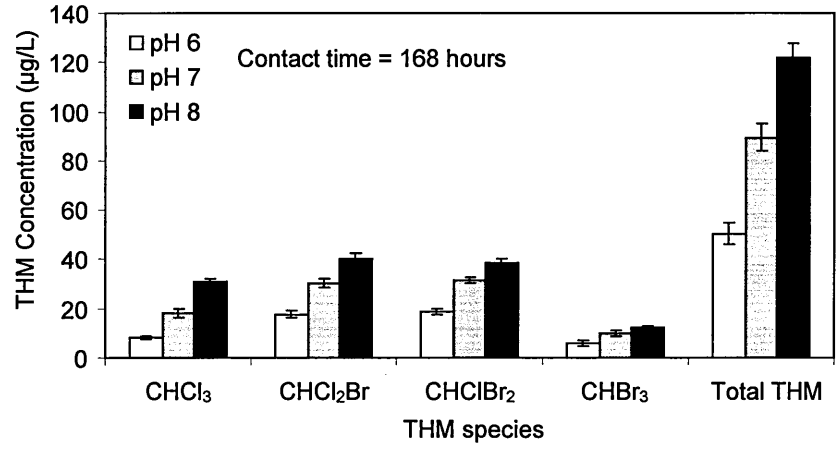

Figure 7. Comparison of pH effect on the formation of THM_4 in the lowland water

Although the trend is similar for both waters, the increase in pH has a greater effect in the lowland water compared to the upland water (THMs increased by 140% and 47% respectively).

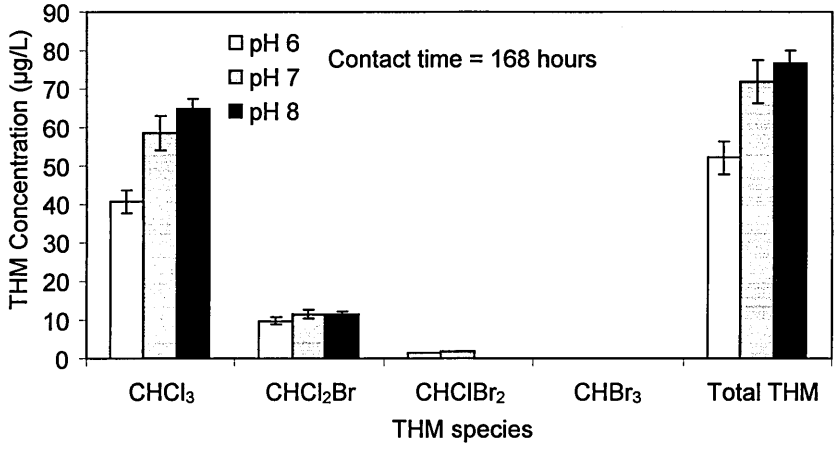

Figure 8. Comparison of pH effect on the formation of THM_4 in the upland water

In 1978, Trussell and Umphres (*33*) reported that the formation of THMs consists of alternate hydrolysis and halogenation steps. All these reactions are favoured under alkaline condition, thus more THMs are formed at higher pH, which is illustrated by the results found here. The impact of pH is limited in the upland water compared to the lowland water which could be explained by the difference of organic matter responsible for the THM formation and its likelihood to undergo hydrolysis and halogenation reactions.

Impact of bromide

The effect of bromide concentration on HAA and THM formation and speciation was investigated by spiking the lowland and the upland water with 200 µg/L of bromide. In the lowland water, the addition of bromide had a slight impact (10% decrease) on the total concentration of HAAs measured. Less DCAA and TCAA are formed (Figure 9), whereas more brominated HAA species are produced.

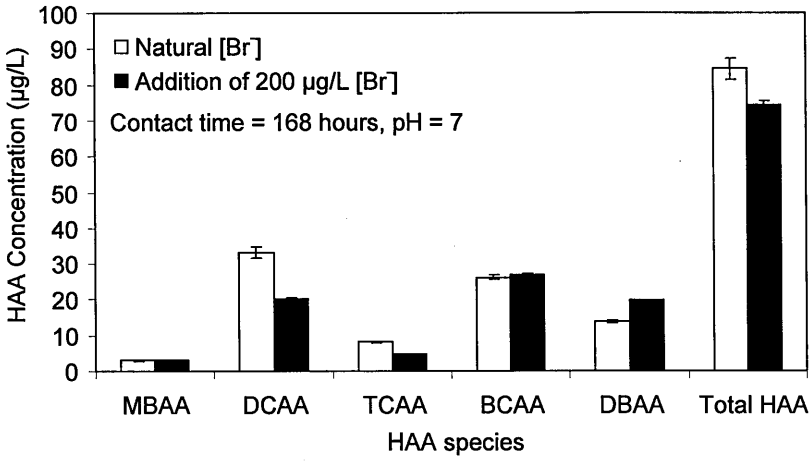

Figure 9. Impact of bromide on the formation of measured HAAs in the lowland water

The addition of bromide had a greater impact in the upland water than in the lowland water (Figure 9 and 10). With the upland water the total concentration of HAAs decreased, but the formation of the chlorinated species DCAA and TCAA was 60% less whereas the concentration of the brominated species MBAA, BCAA and DBAA was 500% greater. It was reported by Hua et al. (*34*) that the total concentration of the five regulated HAAs in the US (MCAA, MBAA, DCAA, TCAA and DBAA) decreased as bromide concentration increased because of the number of brominated species measured. This applies here but the exception is that BCAA is included in the total HAAs and not MCAA. However the same study reported that addition of bromide increased the total HAA_9 (HAA_6, plus bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (DBCAA) and tribromoacetic acid (TBAA)) yield between 0 and 35%.

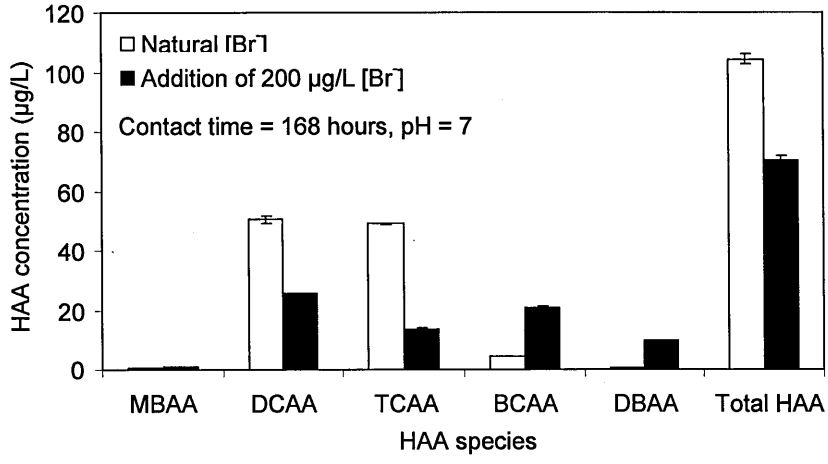

Figure 10. Impact of bromide on the formation of measured HAAs in the upland water

Bromine was reported by Cowman and Singer (*8*) to be more reactive than chlorine in substitution and addition reactions that form HAAs, thus the inclusion of bromine shifts the speciation of the HAA towards the brominated species.

The formation of THM is also affected by the addition of bromide. Hua et al. (*34*) reported that increasing initial bromide levels resulted in a substantially increased THM molar concentration between 14 and 74%. Here the total THM weight concentration increased by 60% in the lowland water (Figure 11) and by 54% in the upland water (Figure 12). Again, the difference of initial bromide concentration could explain the differences observed. In the upland water, only the brominated species increased, whereas all the brominated species and chloroform were slightly augmented in the lowland water.

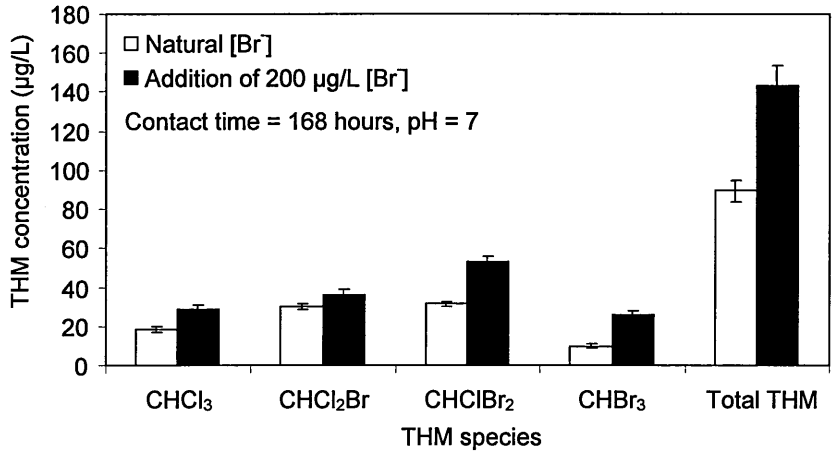

Figure 11. Impact of bromide on the formation of THM_4 in the lowland water

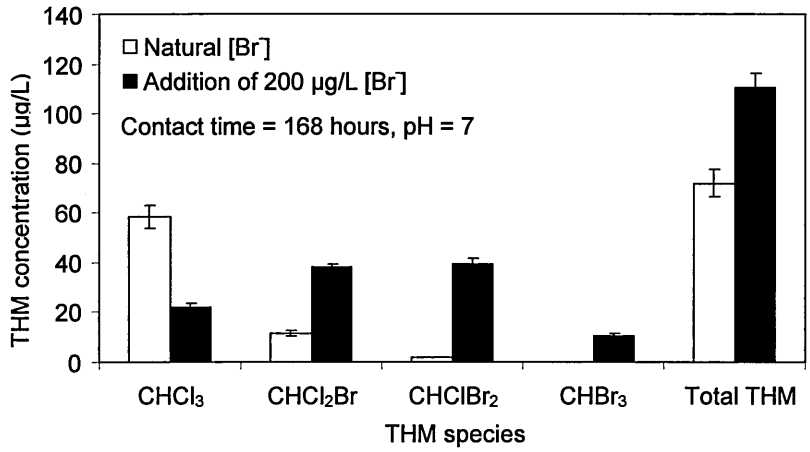

Figure 12. Impact of bromide on the formation of THM_4 in the upland water

Impact of temperature

Reducing the incubation temperature from 20°C to 7°C, resulted in reduction of the concentration of the HAAs and THMs in both waters. The concentration of HAAs and THMs dropped by 59% and 43% respectively in the lowland water after 168 hours of contact time (Figure 13).

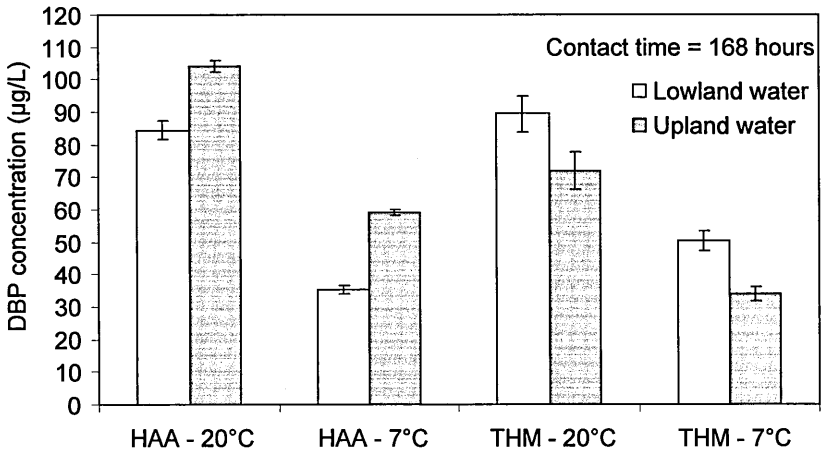

Figure 13. Temperature effect on the DBP formation in lowland and upland water

The same trend was observed with the upland water (Figure 13), where the concentration of HAAs and THMs decreased by 43% and 53% respectively after 168 hours of contact time.

El-Dib and Ali (*32*) reported that the effect of temperature (rise between 0 and 30°C) on the THM yield was rather limited compared with data reported by other investigators (*35*) and concluded that the differences were due to the nature of organic precursors liable to be found in the water.

Dojlido et al. (*36*) reported that the concentrations of HAAs were seasonally dependant. During the winter season (1°C) they found levels of ~ 0.63 µg/mg C whereas in the summer (23°C), concentrations reached ~ 7.4 µg/mg C. In the UK the effect of season on HAA formation has not been determined but the results shown here (Figure 13) indicate there may be a seasonal effect. A UK study by Malliarou et al. (*6*) concluded that THM concentrations were not correlated with temperature but the correlation between HAA levels and temperature was significant. However, no actual temperature values were reported.

Conclusions

Water was collected from two different geographical locations. The upland water NOM was primarily hydrophilic, whereas the lowland water had a higher transphilic content. Both waters exhibited different behaviour to the parameters they were exposed to.

GC-ECD was regarded as the most suitable technology for analysis of HAAs at low µg/L levels. Levels of HAAs were almost identical to the level of THMs in the lowland water, whereas the concentration of HAAs was higher than the concentration of THMs in the upland water.

For both waters, the pH significantly affected THM formation, but had little effect on HAA formation. The greatest pH impact was found in the formation of THMs in the lowland water. It can be concluded that the structure of the precursors is more important when determining HAA formation than the chlorination pH.

Addition of bromide to the water leads to a higher percentage of brominated HAAs and THMs and a total increase in concentration if all THMs and HAAs are measured. The impact on total HAAs will vary depending on the number of brominated species measured.

A reduction in temperature resulted in a major decrease in DBP formation.

The variation in DBP formation by the two waters is believed to be correlated to the difference in THM and HAA precursors liable to be found in each. Future research will focus on DBP formation by each of the isolated fractions. This will give an insight into the specific organics responsible for the DBP formation in UK drinking water. Following this, treatment could be adapted to remove HAA precursors should regulation occur in the UK.

Acknowledgements

This work was funded by Anglian Water, Northumbrian Water Limited, Severn Trent Water, United Utilities, Yorkshire Water Services and the Open University.

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Appendix 5 - Raw Data

The full data for the Kinetic study in Chapter 5 for replicate individual THM and THM4 concentrations individual HAA concentrations from the GC-μECD and GC×GC-ToFMS over the full chlorination contact period.

Table A.9: The concentrations of THMs ($CHCl_3$, $CHCl_2Br$, $CHCl_2Br$, and $CHBr_3$) present, in lowland water, after various periods of chlorination at A) pH 6 B) pH 7 and C) pH 8

A

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	0.32	± 0.08	0.58	± 0.11	0.88	± 0.15	1.16	± 0.38	3.07	± 0.32	4.90	± 0.49	7.97	± 0.62
$CHCl_2Br$	1.12	± 0.40	2.19	± 0.46	2.58	± 0.80	3.76	± 0.37	8.27	± 0.53	11.56	± 1.65	17.75	± 1.57
$CHClBr_2$	2.57	± 0.66	3.00	± 0.69	4.13	± 1.38	6.50	± 0.89	10.88	± 1.77	14.88	± 1.14	18.67	± 1.31
$CHBr_3$	0.40	± 0.12	0.35	± 0.16	0.36	± 0.07	1.51	± 0.95	4.42	± 0.57	5.15	± 1.29	5.91	± 1.01
THM4	4.41	± 0.79	6.13	± 0.85	7.94	± 0.85	12.92	± 1.41	26.65	± 1.97	36.50	± 2.43	50.30	± 2.40

B

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	0.83	± 0.23	1.13	± 0.28	1.45	± 0.21	2.30	± 0.24	6.27	± 0.63	10.88	± 0.81	18.15	± 1.55
$CHCl_2Br$	2.49	± 0.22	3.50	± 0.51	5.20	± 0.42	6.42	± 0.83	14.22	± 0.62	21.06	± 1.13	30.34	± 1.53
$CHClBr_2$	5.14	± 0.61	5.91	± 0.34	9.91	± 0.91	12.12	± 1.26	18.93	± 0.71	26.07	± 1.42	31.27	± 1.16
$CHBr_3$	1.39	± 0.43	2.12	± 0.80	3.66	± 0.79	4.98	± 0.51	6.38	± 0.71	8.81	± 0.87	9.67	± 1.18
THM4	9.85	± 0.81	12.66	± 1.05	20.21	± 1.29	25.82	± 1.61	45.79	± 1.34	66.81	± 2.17	89.43	± 2.74

C

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	14.90	± 1.18	16.18	± 0.77	16.92	± 1.15	20.20	± 0.91	10.01	± 0.55	17.63	± 0.72	31.05	± 1.24
$CHCl_2Br$	3.08	± 0.83	5.63	± 0.72	7.57	± 1.06	10.79	± 0.76	20.13	± 1.15	28.37	± 1.21	40.28	± 2.06
$CHClBr_2$	6.53	± 1.03	9.01	± 0.90	12.35	± 0.94	15.78	± 0.57	25.81	± 2.08	30.85	± 1.05	38.41	± 1.74
$CHBr_3$	3.28	± 0.65	4.35	± 0.85	5.87	± 0.82	7.50	± 0.27	11.75	± 1.31	11.18	± 1.63	12.44	± 0.33
THM4	27.80	± 1.89	35.17	± 1.63	42.71	± 2.00	54.28	± 1.34	67.69	± 2.77	88.03	± 2.39	122.19	± 2.98

Table A.10: The concentrations THMs ($CHCl_3$, $CHCl_2Br$, $CHCl_2Br$, and $CHBr_3$) present, in upland water, after various periods of chlorination at A) pH 6 B) pH 7 and C) pH 8

A

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	4.54	± 0.54	5.53	± 0.36	10.08	± 0.56	11.97	± 0.91	24.28	0.95	33.44	± 1.93	40.67	± 3.06
$CHCl_2Br$	2.37	± 0.29	2.47	± 0.24	4.31	± 0.43	4.80	± 0.44	6.39	0.46	9.25	± 0.87	9.80	± 1.03
$CHClBr_2$	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-
$CHBr_3$	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-
THM4	6.92	± 0.61	8.00	± 0.43	14.39	± 0.70	16.77	± 1.01	30.67	± 1.05	42.69	± 2.12	50.47	± 3.23

B

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	7.41	± 0.25	8.65	± 0.32	15.16	± 0.49	18.29	± 2.66	36.35	± 2.61	47.51	± 1.09	58.43	± 4.53
$CHCl_2Br$	3.22	± 0.41	3.71	± 0.14	5.68	± 0.37	6.77	± 0.62	8.93	± 0.64	11.01	± 0.46	11.63	± 1.12
$CHClBr_2$	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-
$CHBr_3$	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-
THM4	10.63	± 0.48	12.36	± 0.34	20.84	± 0.61	25.06	± 2.73	45.29	± 2.69	58.52	± 1.18	70.06	± 4.67

C

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	8.29	± 0.81	14.21	± 1.12	21.26	± 1.81	28.32	± 0.99	40.95	± 1.63	56.33	± 3.72	67.01	2.59
$CHCl_2Br$	3.66	± 0.55	5.04	± 0.99	6.98	± 1.18	8.87	± 0.50	10.20	± 0.67	10.68	± 0.59	11.97	0.63
$CHClBr_2$	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-
$CHBr_3$	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-	nd	-
THM4	11.95	± 0.98	19.25	± 1.50	28.24	± 2.16	37.19	± 1.11	51.16	± 1.76	67.00	± 3.77	78.98	± 2.67

Table A.11: The concentrations THMs (CHCl3, CHCl2Br, CHCl2Br, and CHBr3) present at various periods of chlorination at A) lowland water B) upland water the after addition of bromide (200 µg/l).

A

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	16.14	± 1.26	15.00	± 1.09	18.83	± 1.23	19.17	± 1.87	19.98	± 0.73	24.28	± 1.37	28.51	± 2.31
$CHCl_2Br$	1.90	± 0.65	2.68	± 0.28	4.99	± 0.33	7.06	± 0.65	13.72	± 0.81	24.33	± 1.82	36.10	± 2.64
$CHClBr_2$	5.29	± 0.61	6.33	± 0.89	12.13	± 0.86	16.31	± 1.45	24.49	± 1.41	38.36	± 2.12	52.88	± 3.13
$CHBr_3$	6.87	± 2.10	6.34	± 0.80	9.13	± 1.66	10.05	± 1.62	15.64	± 1.39	21.41	± 1.56	25.80	± 2.00
THM4	30.21	± 2.60	30.35	± 1.64	45.08	± 2.26	52.58	± 2.94	73.83	± 2.26	108.39	± 3.48	143.29	± 5.11

B

	0.5 hr	σ_{n-1}	1 hr	σ_{n-1}	3 hr	σ_{n-1}	6 hr	σ_{n-1}	24 hr	σ_{n-1}	72 hr	σ_{n-1}	168 hr	σ_{n-1}
$CHCl_3$	2.53	± 0.27	3.17	± 0.62	4.77	± 0.34	6.45	± 0.93	10.86	± 0.57	17.62	± 0.85	22.25	± 1.35
$CHCl_2Br$	6.54	± 0.35	6.59	± 0.55	11.30	± 0.48	14.75	± 1.22	22.30	± 0.71	32.45	± 1.69	38.19	± 1.37
$CHClBr_2$	9.16	± 0.97	8.87	± 0.57	16.72	± 1.00	20.38	± 1.78	25.98	± 1.64	34.72	± 2.36	39.59	± 1.88
$CHBr_3$	5.38	± 1.77	9.27	± 4.32	6.27	± 1.16	8.22	± 1.04	9.32	± 1.24	11.79	± 2.11	10.70	± 0.92
THM4	23.60	± 2.07	27.89	± 4.43	39.06	± 1.65	49.79	± 2.58	68.47	± 2.25	96.58	± 3.69	110.73	± 2.84

MCAA Concentrations - Lowland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Lowland pH 6								
0.5	0.92	0.69	0.81	0.12	1.42	1.20	1.31	0.11
1	13.73	5.88	9.81	3.93	13.19	2.29	7.74	5.45
3	2.15	1.85	2.00	0.15	2.18	2.44	2.31	0.13
6	0.99	0.91	0.95	0.04	n/d	0.72	0.72	-
24	18.74	5.09	11.92	6.83	17.62	2.13	9.88	7.75
72	6.47	11.43	8.95	2.48	n/r	9.39	9.39	-
168	10.98	13.06	12.02	1.04	2.54	4.76	3.65	1.11
Lowland pH 7								
0.5	0.82	0.53	0.68	0.15	n/d	n/d	-	-
1	2.96	2.80	2.88	0.08	n/d	n/d	-	-
3	3.13	1.34	2.24	0.90	n/d	n/d	-	-
6	4.11	5.90	5.01	0.90	n/d	0.40	0.40	-
24	14.66	5.05	9.86	4.81	3.15	1.38	2.27	0.89
72	10.25	8.53	9.39	0.86	3.05	3.22	3.14	0.09
168	8.85	15.82	12.34	3.49	4.44	3.31	3.88	0.57
Lowland pH 8								
0.5	18.99	5.53	12.26	6.73	22.62	8.50	15.56	7.06
1	5.25	11.37	8.31	3.06	8.55	15.17	11.86	3.31
3	31.23	10.37	20.80	10.43	31.58	8.60	20.09	11.49
6	40.91	98.27	69.59	28.68	41.27	114.12	77.70	36.43
24	3.28	9.98	6.63	3.35	11.22	9.83	10.53	0.70
72	16.12	43.16	29.64	13.52	19.43	30.43	24.93	5.50
168	16.74	12.16	14.45	2.29	15.80	11.19	13.50	2.31
Lowland + Br								
0.5	0.76	1.10	0.93	0.17	0.89	0.39	0.64	0.25
1	1.59	6.07	3.83	2.24	3.40	3.95	3.68	0.28
3	2.97	2.13	2.55	0.42	0.42	0.91	0.67	0.25
6	7.18	7.40	7.29	0.11	1.21	0.41	0.81	0.40
24	18.12	5.16	11.64	6.48	1.78	0.34	1.06	0.72
72	5.65	5.41	5.53	0.12	2.37	3.63	3.00	0.63
168	28.65	41.32	34.98	6.34	7.28	5.48	6.38	0.90

MCAA Concentrations - Upland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Upland pH 6								
0.5	18.02	9.72	13.87	4.15	4.46	4.33	4.40	0.06
1	12.63	8.46	10.54	2.09	5.74	5.10	5.42	0.32
3	22.64	10.06	16.35	6.29	12.24	4.21	8.23	4.02
6	126.32	15.58	70.95	55.37	127.16	10.87	69.02	58.15
24	28.25	20.42	24.34	3.92	3.50	8.46	5.98	2.48
72	24.92	28.70	26.81	1.89	2.05	15.89	8.97	6.92
168	25.61	70.82	48.22	22.60	8.12	51.33	29.73	21.61
Upland pH 7								
0.5	14.40	24.42	19.41	5.01	10.14	9.47	9.81	0.34
1	15.30	17.55	16.43	1.13	3.31	2.20	2.76	0.56
3	60.31	14.11	37.21	23.10	30.43	4.69	17.56	12.87
6	19.59	17.19	18.39	1.20	7.90	5.74	6.82	1.08
24	20.81	78.97	49.89	29.08	7.31	68.19	37.75	30.44
72	33.92	34.24	34.08	0.16	6.99	9.56	8.28	1.29
168	27.91	30.06	28.99	1.07	7.53	4.15	5.84	1.69
Upland pH 8								
0.5	6.96	8.15	7.56	0.60	3.18	3.37	3.28	0.10
1	15.43	12.53	13.98	1.45	3.07	2.60	2.84	0.24
3	25.77	13.95	19.86	5.91	3.46	–	3.46	–
6	35.65	25.72	30.69	4.97	1.81	3.46	2.64	0.83
24	29.37	42.59	35.98	6.61	–	1.65	1.65	–
72	40.84	82.66	61.75	20.91	–	8.29	8.29	–
168	28.96	33.57	31.27	2.31	4.55	7.99	6.27	–
Upland + Br								
0.5	1.16	0.00	0.58	0.58	0.75	1.62	1.19	0.44
1	19.52	3.74	11.63	7.89	5.26	21.52	13.39	8.13
3	6.20	0.00	3.10	3.10	3.27	3.53	3.40	0.13
6	0.00	10.61	5.31	5.31	1.91	2.90	2.41	0.50
24	21.97	29.37	25.67	3.70	3.05	3.76	3.41	0.36
72	36.31	12.97	24.64	11.67	4.13	14.50	9.32	5.19
168	19.50	10.64	15.07	4.43	4.25	5.96	5.11	0.86

MBAA Concentrations - Lowland Water

Contact Time (hr)	GC-μECD				GCxGC-TOFMS			
	Sample 1	Sample 2	Mean	Variance	Sample 1	Sample 2	Mean	Variance
Lowland pH 6								
0.5	0.33	0.35	0.34	0.01	n/d	n/d	–	–
1	0.36	0.36	0.36	0.00	n/d	n/d	–	–
3	0.67	0.70	0.69	0.02	0.60	0.59	0.60	0.01
6	0.86	0.72	0.79	0.07	0.75	0.54	0.65	0.11
24	1.45	1.53	1.49	0.04	1.81	1.28	1.55	0.27
72	1.89	1.73	1.81	0.08	n/r	2.65	2.65	0.00
168	2.81	2.71	2.76	0.05	2.62	2.69	2.66	0.03
Lowland pH 7								
0.5	0.44	0.43	0.44	0.01	n/d	n/d	–	–
1	0.50	0.55	0.53	0.03	n/d	n/d	–	–
3	0.67	0.73	0.70	0.03	n/d	n/d	–	–
6	0.95	0.97	0.96	0.01	0.76	0.73	0.75	0.02
24	1.27	1.44	1.36	0.09	2.77	1.34	2.06	0.72
72	1.98	2.17	2.08	0.10	1.17	1.02	1.10	0.08
168	3.02	2.97	3.00	0.02	1.88	2.11	2.00	0.12
Lowland pH 8								
0.5	0.53	0.55	0.54	0.01	n/d	n/d	–	–
1	0.50	0.64	0.57	0.07	0.9	0.75	0.83	0.08
3	0.91	0.94	0.92	0.02	0.9	0.92	0.91	0.01
6	0.69	0.83	0.76	0.07	1.25	0.81	1.03	0.22
24	1.21	1.31	1.26	0.05	1.64	0.78	1.21	0.43
72	1.81	1.61	1.71	0.10	1.32	1.83	1.58	0.26
168	2.53	2.20	2.36	0.17	3.14	2.36	2.75	0.39
Lowland + Br								
0.5	0.47	0.46	0.47	0.00	n/d	n/d	–	–
1	0.51	0.66	0.59	0.08	n/d	n/d	–	–
3	0.65	0.67	0.66	0.01	n/d	n/d	–	–
6	0.84	0.96	0.90	0.06	n/d	n/d	–	–
24	1.27	1.41	1.34	0.07	1.33	1.13	1.23	0.10
72	2.28	1.89	2.08	0.19	1.52	2.06	1.79	0.27
168	3.05	3.22	3.13	0.09	2.51	4.79	3.65	1.14

MBAA Concentrations - Upland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Upland pH 6								
0.5	0.14	0.17	0.15	0.02	n/d	n/d	–	–
1	0.00	0.11	0.05	0.05	n/d	n/d	–	–
3	0.00	0.14	0.07	0.07	n/d	n/d	–	–
6	0.29	0.15	0.22	0.07	n/d	n/d	–	–
24	0.00	0.24	0.12	0.12	n/d	n/d	–	–
72	0.26	0.43	0.35	0.09	n/d	n/d	–	–
168	0.31	0.48	0.40	0.09				
Upland pH 7								
0.5	0.00	0.00	0.00	0.00	n/d	n/d	–	–
1	0.09	0.26	0.17	0.08	n/d	n/d	–	–
3	0.25	0.18	0.21	0.04	n/d	n/d	–	–
6	0.19	0.18	0.18	0.00	n/d	n/d	–	–
24	0.24	0.31	0.28	0.04	n/d	n/d	–	–
72	0.28	0.30	0.29	0.01	n/d	n/d	–	–
168	0.30	0.30	0.30	0.00				
Upland pH 8								
0.5	0.23	0.34	0.29	0.06	n/d	n/d	–	–
1	0.27	0.18	0.23	0.05	n/d	n/d	–	–
3	0.32	0.24	0.28	0.04	n/d	n/d	–	–
6	0.28	0.30	0.29	0.01	n/d	n/d	–	–
24	0.33	0.31	0.32	0.01	n/d	n/d	–	–
72	0.47	0.40	0.44	0.04	n/d	n/d	–	–
168	0.48	0.42	0.45	0.03	n/d	n/d	–	–
Upland + Br								
0.5	0.27	0.36	0.31	0.04	n/d	n/d	–	–
1	0.52	0.37	0.45	0.07	n/d	n/d	–	–
3	0.47	0.52	0.49	0.02	n/d	n/d	–	–
6	0.50	0.58	0.54	0.04	n/d	n/d	–	–
24	0.62	0.67	0.64	0.02	n/d	n/d	–	–
72	0.94	1.02	0.98	0.04	0.56	0.32	0.44	0.12
168	1.09	1.13	1.11	0.02	0.72	0.94	0.83	0.11

DCAA Concentrations - Lowland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	Sample 1	Sample 2	Mean	Variance	Sample 1	Sample 2	Mean	Variance
Lowland pH 6								
0.5	4.00	3.75	3.88	0.13	2.15	1.94	2.05	0.11
1	4.35	4.66	4.51	0.16	2.78	3.00	2.89	0.11
3	6.19	6.55	6.37	0.18	3.52	3.81	3.67	0.15
6	6.96	6.97	6.97	0.00	3.50	3.46	3.48	0.02
24	12.07	12.98	12.53	0.46	7.36	6.68	7.02	0.34
72	21.40	19.82	20.61	0.79	n/r	10.54	10.54	0.00
168	30.32	28.71	29.52	0.81	14.14	14.53	14.34	0.19
Lowland pH 7								
0.5	5.74	6.06	5.90	0.16	3.60	5.08	4.34	0.74
1	4.67	5.1	4.89	0.22	3.45	4.01	3.73	0.28
3	6.31	5.82	6.07	0.25	4.34	2.87	3.61	0.74
6	6.65	6.78	6.72	0.06	5.62	5.12	5.37	0.25
24	14.27	12.54	13.41	0.87	9.54	8.03	8.79	0.76
72	21.34	20.7	21.02	0.32	12.79	13.50	13.15	0.36
168	32.15	34.41	33.28	1.13	21.42	19.77	20.60	0.83
Lowland pH 8								
0.5	2.34	2.46	2.40	0.06	1.71	1.8	1.76	0.05
1	3.04	3.59	3.32	0.28	1.83	2.56	2.20	0.37
3	4.05	4.33	4.19	0.14	3.06	3.43	3.25	0.19
6	5.49	5.07	5.28	0.21	4.21	3.99	4.10	0.11
24	9.48	9.81	9.65	0.17	8.20	8.19	8.20	0.00
72	14.95	14.55	14.75	0.20	13.62	11.32	12.47	1.15
168	24.70	21.95	23.33	1.38	20.89	19.29	20.09	0.80
Lowland + Br								
0.5	1.77	1.83	1.80	0.03	1.15	0.76	0.96	0.20
1	1.80	2.33	2.06	0.27	1.06	1.61	1.34	0.28
3	2.87	2.68	2.78	0.09	2.01	1.81	1.91	0.10
6	3.90	4.21	4.05	0.16	2.83	2.38	2.61	0.23
24	8.65	7.56	8.10	0.54	5.3	2.34	3.82	1.48
72	14.33	14.34	14.33	0.00	7.4	8.81	8.11	0.71
168	20.40	20.09	20.24	0.15	12.77	13.63	13.20	0.43

DCAA Concentrations - Upland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Upland pH 6								
0.5	18.80	11.54	15.17	3.63	11.20	6.76	8.98	2.22
1	12.59	12.78	12.69	0.10	6.65	7.41	7.03	0.38
3	17.35	17.44	17.40	0.05	9.29	10.36	9.83	0.54
6	20.67	19.95	20.31	0.36	13.21	11.02	12.12	1.10
24	32.56	34.94	33.75	1.19	17.52	18.67	18.10	0.58
72	45.34	44.57	44.96	0.39	25.27	22.94	24.11	1.17
168	59.15	60.63	59.89	0.74	30.12	29.14	29.63	0.49
Upland pH 7								
0.5	11.30	12.21	11.76	0.45	6.94	7.14	7.04	0.10
1	12.89	18.35	15.62	2.73	7.21	7.00	7.11	0.11
3	18.69	18.29	18.49	0.20	10.04	10.11	10.08	0.04
6	20.30	20.23	20.26	0.03	12.33	10.26	11.30	1.04
24	30.55	30.76	30.66	0.10	18.02	19.90	18.96	0.94
72	43.21	43.10	43.15	0.05	25.05	25.44	25.25	0.20
168	51.33	49.40	50.36	0.96	33.86	30.20	32.03	1.83
Upland pH 8								
0.5	17.11	16.83	16.97	0.14	11.49	11.14	11.32	0.18
1	18.08	18.95	18.52	0.44	13.95	10.88	12.42	1.54
3	21.33	21.11	21.22	0.11	13.34	12.83	13.09	0.26
6	25.32	25.57	25.45	0.13	17.26	13.95	15.61	1.66
24	32.75	32.09	32.42	0.33	13.12	20.72	16.92	3.80
72	39.51	42.03	40.77	1.26	23.57	32.10	27.84	4.27
168	54.99	50.37	52.68	2.31	39.87	47.92	43.90	4.03
Upland + Br								
0.5	4.85	4.91	4.88	0.03	3.19	3.56	3.38	0.19
1	5.53	5.10	5.31	0.21	2.93	3.23	3.08	0.15
3	7.55	8.22	7.88	0.34	4.15	5.42	4.79	0.64
6	8.73	10.23	9.48	0.75	4.67	7.55	6.11	1.44
24	14.74	15.65	15.19	0.46	9.34	10.33	9.84	0.50
72	21.07	20.61	20.84	0.23	12.56	13.61	13.09	0.52
168	24.30	24.51	24.41	0.10	12.77	15.73	14.25	1.48

TCAA Concentrations - Lowland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Lowland pH 6								
0.5	1.97	1.87	1.92	0.05	2.09	1.92	2.01	0.09
1	2.12	2.18	2.15	0.03	2.05	1.99	2.02	0.03
3	2.44	2.77	2.61	0.17	2.55	2.55	2.55	0.00
6	2.88	2.63	2.76	0.13	2.53	2.58	2.56	0.03
24	4.53	4.93	4.73	0.20	4.75	4.83	4.79	0.04
72	7.07	6.89	6.98	0.09	n/r	8.47	8.47	0.00
168	10.18	10.64	10.41	0.23	10.17	10.02	10.10	0.08
Lowland pH 7								
0.5	1.32	1.26	1.29	0.03	1.3	1.65	1.48	0.18
1	1.42	1.3	1.36	0.06	1.43	1.51	1.47	0.04
3	1.53	1.56	1.55	0.02	1.75	1.83	1.79	0.04
6	2.00	2.01	2.01	0.00	1.78	2.09	1.94	0.16
24	3.74	2.96	3.35	0.39	4.07	3.54	3.81	0.27
72	4.16	4.52	4.34	0.18	4.14	5.00	4.57	0.43
168	8.22	8.07	8.15	0.08	8.78	7.42	8.10	0.68
Lowland pH 8								
0.5	1.21	1.32	1.26	0.06	1.33	1.51	1.42	0.09
1	1.22	1.66	1.44	0.22	1.47	1.89	1.68	0.21
3	1.80	1.72	1.76	0.04	2.06	1.55	1.81	0.26
6	1.94	2.18	2.06	0.12	2.51	2.47	2.49	0.02
24	3.59	3.47	3.53	0.06	4.01	3.65	3.83	0.18
72	4.86	5.00	4.93	0.07	5.09	3.71	4.40	0.69
168	8.13	6.55	7.34	0.79	10.57	7.93	9.25	1.32
Lowland + Br								
0.5	0.48	0.66	0.57	0.09	0.52	0.61	0.57	0.05
1	0.78	0.93	0.86	0.08	0.75	2.09	1.42	0.67
3	0.84	0.94	0.89	0.05	0.92	0.86	0.89	0.03
6	1.16	1.12	1.14	0.02	1.24	1.49	1.37	0.13
24	2.12	1.48	1.80	0.32	2.27	1.01	1.64	0.63
72	2.44	2.54	2.49	0.05	2.82	3.97	3.40	0.58
168	4.39	4.78	4.59	0.19	5.44	6.5	5.97	0.53

TCAA Concentrations - Upland Water

Contact Time (hr)	GC-μECD				GCxGC-TOFMS			
	Sample 1	Sample 2	Mean	Variance	Sample 1	Sample 2	Mean	Variance
Upland pH 6								
0.5	13.73	7.80	10.76	2.97	15.72	9.64	12.68	3.04
1	8.80	9.09	8.94	0.14	9.93	10.00	9.97	0.04
3	13.56	13.36	13.46	0.10	14.50	15.19	14.85	0.35
6	17.11	16.84	16.97	0.14	18.68	17.56	18.12	0.56
24	31.36	32.47	31.91	0.56	37.16	31.94	34.55	2.61
72	42.24	39.97	41.10	1.13	41.02	43.86	42.44	1.42
168	51.64	51.75	51.69	0.05	49.61	48.81	49.21	0.40
Upland pH 7								
0.5	8.10	8.16	8.13	0.03	8.90	9.54	9.22	0.32
1	9.68	10.77	10.23	0.54	9.17	8.93	9.05	0.12
3	16.56	14.13	15.34	1.21	16.44	15.95	16.20	0.25
6	21.14	19.41	20.27	0.87	20.27	18.00	19.14	1.14
24	30.22	30.73	30.48	0.26	29.29	32.39	30.84	1.55
72	43.18	40.74	41.96	1.22	37.68	37.24	37.46	0.22
168	48.79	49.14	48.97	0.18	50.73	46.67	48.70	2.03
Upland pH 8								
0.5	8.69	8.39	8.54	0.15	12.79	11.57	12.18	0.61
1	12.34	12.83	12.59	0.25	17.63	16.49	17.06	0.57
3	19.13	18.40	18.77	0.37	22.50	19.82	21.16	1.34
6	23.91	25.90	24.91	0.99	28.74	28.13	28.44	0.31
24	39.78	40.90	40.34	0.56	40.57	45.15	42.86	2.29
72	56.00	60.12	58.06	2.06	49.58	57.74	53.66	4.08
168	73.76	73.10	73.43	0.33	69.17	71.97	70.57	1.40
Upland + Br								
0.5	1.96	2.04	2.00	0.04	2.14	2.42	2.28	0.14
1	3.03	2.77	2.90	0.13	3.47	3.78	3.63	0.16
3	3.81	4.07	3.94	0.13	4.27	4.04	4.16	0.12
6	4.78	5.34	5.06	0.28	7.00	5.37	6.19	0.82
24	7.95	8.55	8.25	0.30	8.44	8.31	8.38	0.06
72	11.48	11.03	11.26	0.23	10.25	11.64	10.95	0.70
168	13.22	12.56	12.89	0.33	13.23	13.62	13.43	0.19

BCAA Concentrations - Lowland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Lowland pH 6								
0.5	3.24	2.82	3.03	0.21	2.35	2.2	2.28	0.08
1	3.49	3.64	3.57	0.08	3.97	3.48	3.73	0.25
3	7.69	7.46	7.58	0.12	7.41	7.41	7.41	0.00
6	9.37	9.24	9.31	0.06	9.24	8.29	8.77	0.48
24	15.21	16.38	15.80	0.58	16.49	14.65	15.57	0.92
72	22.30	21.07	21.69	0.62	n/r	21.05	21.05	0.00
168	26.02	25.49	25.76	0.27	22.69	25.16	23.93	1.24
Lowland pH 7								
0.5	1.90	2.16	2.03	0.13	1.48	2.03	1.76	0.28
1	2.20	2.26	2.23	0.03	2.52	1.90	2.21	0.31
3	4.48	4.65	4.57	0.09	4.30	4.02	4.16	0.14
6	5.58	6.03	5.81	0.23	6.64	6.00	6.32	0.32
24	10.13	10.46	10.30	0.17	11.82	12.23	12.03	0.21
72	16.28	16.43	16.36	0.07	17.31	19.15	18.23	0.92
168	26.74	25.83	26.29	0.46	26.98	27.31	27.15	0.16
Lowland pH 8								
0.5	2.46	2.58	2.52	0.06	2.25	2.28	2.27	0.01
1	3.08	3.31	3.19	0.11	2.38	2.63	2.51	0.13
3	4.50	5.01	4.75	0.25	4.52	5.39	4.96	0.44
6	5.95	5.85	5.90	0.05	5.48	5.31	5.40	0.09
24	9.78	10.21	9.99	0.21	10.14	10.77	10.46	0.32
72	14.87	14.51	14.69	0.18	15.37	17.59	16.48	1.11
168	21.80	20.11	20.95	0.84	21.75	20.74	21.25	0.51
Lowland + Br								
0.5	1.78	1.97	1.88	0.10	1.18	1.97	1.58	0.40
1	2.11	2.44	2.28	0.16	1.88	3.5	2.69	0.81
3	4.22	4.37	4.30	0.07	4.68	5.11	4.90	0.22
6	6.09	6.50	6.30	0.21	5.62	5.65	5.64	0.02
24	12.90	11.37	12.14	0.77	12.93	16.84	14.89	1.96
72	21.43	21.05	21.24	0.19	19.93	21.46	20.70	0.77
168	27.07	26.52	26.80	0.27	30.24	29.02	29.63	0.61

BCAA Concentrations - Upland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	**Sample 1**	**Sample 2**	**Mean**	**Variance**	**Sample 1**	**Sample 2**	**Mean**	**Variance**
Upland pH 6								
0.5	1.44	0.97	1.21	0.23	0.94	0.60	0.77	0.17
1	0.99	1.00	1.00	0.00	0.43	0.55	0.49	0.06
3	1.64	1.54	1.59	0.05	1.06	1.18	1.12	0.06
6	1.79	1.72	1.75	0.03	1.66	1.12	1.39	0.27
24	3.00	2.97	2.98	0.01	2.87	2.32	2.60	0.28
72	3.65	3.55	3.60	0.05	3.01	3.20	3.11	0.10
168	4.01	4.25	4.13	0.12	3.60	3.39	3.50	0.11
Upland pH 7								
0.5	1.03	1.01	1.02	0.01	0.99	0.69	0.84	0.15
1	1.20	1.70	1.45	0.25	0.96	0.78	0.87	0.09
3	1.91	1.78	1.84	0.06	1.49	2.29	1.89	0.40
6	2.04	2.03	2.04	0.01	1.54	1.56	1.55	0.01
24	2.85	2.88	2.87	0.01	2.73	2.69	2.71	0.02
72	3.78	3.80	3.79	0.01	2.54	3.25	2.90	0.36
168	4.46	4.33	4.40	0.07	3.86	4.26	4.06	0.20
Upland pH 8								
0.5	1.34	1.41	1.38	0.03	1.27	1.26	1.27	0.01
1	1.72	1.80	1.76	0.04	1.75	1.31	1.53	0.22
3	2.21	2.14	2.18	0.03	1.52	1.46	1.49	0.03
6	2.71	2.71	2.71	0.00	2.75	2.92	2.84	0.09
24	3.56	3.50	3.53	0.03	2.64	3.45	3.05	0.41
72	4.84	5.16	5.00	0.16	4.00	5.10	4.55	0.55
168	5.81	6.29	6.05	0.24	5.92	6.08	6.00	0.08
Upland + Br								
0.5	3.50	3.57	3.54	0.03	2.95	3.58	3.27	0.32
1	3.77	3.18	3.47	0.29	2.41	3.01	2.71	0.30
3	6.54	7.38	6.96	0.42	5.79	6.96	6.38	0.59
6	7.15	8.98	8.07	0.91	7.37	9.51	8.44	1.07
24	12.69	13.47	13.08	0.39	12.17	13.32	12.75	0.58
72	16.40	16.59	16.50	0.10	15.34	16.68	16.01	0.67
168	19.68	20.25	19.97	0.28	16.44	19.23	17.84	1.40

DBAA Concentrations - Lowland Water

	GC-μECD				GCxGC-TOFMS			
Contact Time (hr)	Sample 1	Sample 2	Mean	Variance	Sample 1	Sample 2	Mean	Variance
Lowland pH 6								
0.5	1.61	1.42	1.52	0.10	1.05	1.5	1.28	0.23
1	1.44	1.53	1.49	0.05	1.31	2.18	1.75	0.44
3	3.20	3.03	3.12	0.09	3.21	3.74	3.48	0.27
6	3.88	3.79	3.84	0.04	3.06	4.19	3.63	0.57
24	6.44	6.98	6.71	0.27	7.63	7.19	7.41	0.22
72	9.54	9.13	9.34	0.20	n/r	10.88	10.88	0.00
168	11.77	11.21	11.49	0.28	11.5	12.1	11.80	0.30
Lowland pH 7								
0.5	1.46	1.6	1.53	0.07	1.22	2.12	1.67	0.45
1	1.62	1.71	1.67	0.04	1.55	2.46	2.01	0.46
3	3.30	3.24	3.27	0.03	4.22	4.13	4.18	0.04
6	3.93	4.06	4.00	0.06	5.32	5.08	5.20	0.12
24	5.61	6.66	6.14	0.53	4.63	8.6	6.62	1.99
72	8.73	9.43	9.08	0.35	10.13	11.7	10.92	0.78
168	13.40	14.07	13.74	0.34	16.67	15.17	15.92	0.75
Lowland pH 8								
0.5	2.64	2.76	2.70	0.06	2.99	2.76	2.88	0.12
1	3.27	3.42	3.35	0.08	2.55	3.08	2.82	0.27
3	4.62	4.95	4.78	0.16	4.29	6.11	5.20	0.91
6	5.13	5.06	5.10	0.03	5.98	6.06	6.02	0.04
24	7.78	7.98	7.88	0.10	9.62	9.26	9.44	0.18
72	10.68	10.42	10.55	0.13	12.23	12.22	12.23	0.00
168	13.73	13.23	13.48	0.25	17.39	15.09	16.24	1.15
Lowland + Br								
0.5	1.79	1.91	1.85	0.06	1.48	2.53	2.01	0.53
1	2.07	2.03	2.05	0.02	2.15	2.71	2.43	0.28
3	3.94	3.95	3.95	0.00	4.05	4.58	4.32	0.27
6	5.18	5.47	5.33	0.15	6.17	5.73	5.95	0.22
24	9.49	9.24	9.36	0.13	10.41	18.17	14.29	3.88
72	16.03	15.26	15.64	0.38	16.44	15.73	16.09	0.36
168	19.78	19.60	19.69	0.09	21.91	24.3	23.11	1.20

DBAA Concentrations - Upland Water

Contact Time (hr)	GC-μECD				GC×GC-TOFMS			
	Sample 1	Sample 2	Mean	Variance	Sample 1	Sample 2	Mean	Variance
Upland pH 6								
0.5	0.15	0.11	0.13	0.02	n/d	n/d	–	–
1	0.11	0.11	0.11	0.00	n/d	n/d	–	–
3	0.10	0.11	0.11	0.01	n/d	n/d	–	–
6	0.11	0.14	0.12	0.01	n/d	n/d	–	–
24	0.16	0.19	0.17	0.02	n/d	n/d	–	–
72	0.22	0.18	0.20	0.02	n/d	n/d	–	–
168	0.24	0.24	0.24	0.00	n/d	n/d	–	–
Upland pH 7								
0.5	0.11	0.12	0.12	0.01	n/d	n/d	–	–
1	0.08	0.14	0.11	0.03	n/d	n/d	–	–
3	0.15	0.14	0.15	0.00	n/d	n/d	–	–
6	0.13	0.15	0.14	0.01	n/d	n/d	–	–
24	0.18	0.22	0.20	0.02	n/d	n/d	–	–
72	0.23	0.24	0.23	0.00	n/d	n/d	–	–
168	0.25	0.24	0.25	0.01	n/d	n/d	–	–
Upland pH 8								
0.5	0.23	0.25	0.24	0.01	n/d	n/d	–	–
1	0.23	0.21	0.22	0.01	n/d	n/d	–	–
3	0.25	0.24	0.25	0.01	n/d	n/d	–	–
6	0.29	0.28	0.29	0.00	n/d	n/d	–	–
24	0.32	0.36	0.34	0.02	n/d	n/d	–	–
72	0.41	0.44	0.43	0.02	n/d	n/d	–	–
168	0.46	0.49	0.48	0.02	n/d	n/d	–	–
Upland + Br								
0.5	1.74	1.95	1.84	0.10	2.18	2.04	2.11	0.07
1	1.66	1.58	1.62	0.04	1.81	1.22	1.52	0.30
3	3.05	3.31	3.18	0.13	2.68	3.33	3.01	0.33
6	3.72	4.08	3.90	0.18	3.38	4.54	3.96	0.58
24	5.93	5.91	5.92	0.01	6.18	6.72	6.45	0.27
72	7.65	8.03	7.84	0.19	8.22	8.59	8.41	0.19
168	8.97	9.22	9.10	0.12	8.23	9.87	9.05	0.82

Appendix 6 - Photographs of analytical instrumentation

Below are photographs of some of the analytical systems used for the analysis of THMs and HAAs which are reported in the thesis.

Figure A.4: A Varian CP-3800 gas chromatograph interfaced with a Saturn-2000 ion trap mass spectrometer, and a CTC Combi Pal autosampler were used for the analysis of THMs.

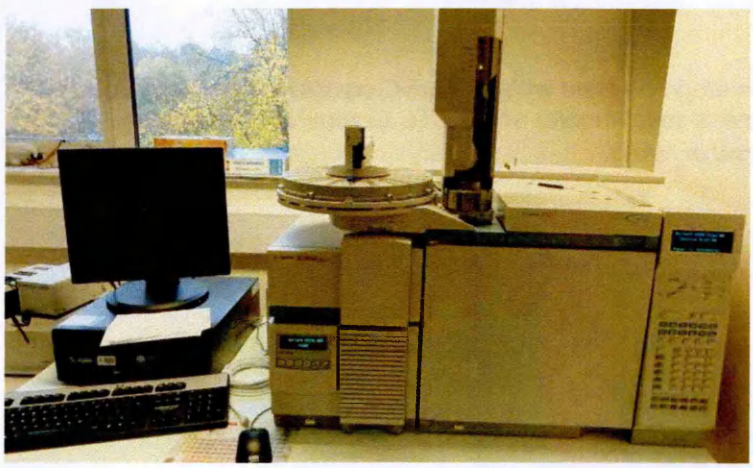

Figure A.5: An Agilent 6890 N GC-μECD fitted with an Agilent 7673 liquid autosampler was utilised for the analysis of HAAs and THMs (in LLE).

Figure A.6: An Agilent 7890 N interfaced with a 5975 quadrupole mass spectrometer and a CTC CombiPal autosampler that was utilised for the analysis of HAAs in electron capture negative ionisation.

Figure A.7: Agilent 6890 N gas chromatograph fitted with a GC×GC cryogenic modulator coupled to a Leco Pegasus IV time-of-flight mass spectrometer and a CTC CombiPal autosampler (GC×GC-ToFMS) used for the analysis of HAAs.

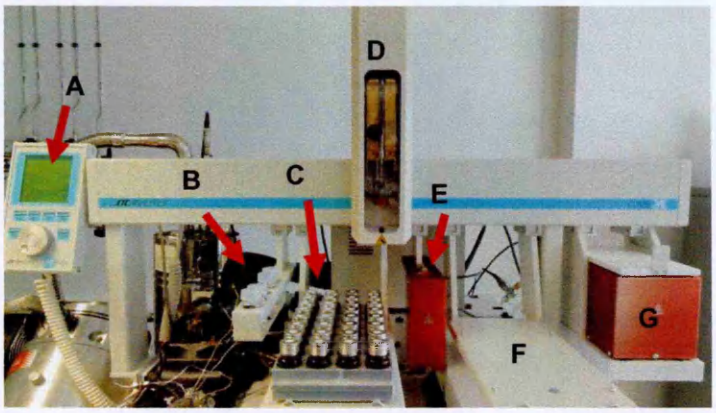

Figure A.8: The CTC CombiPal autosampler with the A) control unit for manual settings, B) solvent wash station, C) tray holder 1 with 32 vial tray capacity for 10 ml and 20 ml vials, D) SPME syringe unit attached, E) SPME fibre cleaning and conditioning station F) tray holder 2, and G) vial incubator and shaker. This autosapler was used for the analysis of THMs and HAAs on various methods, as reported in Chapter 3.

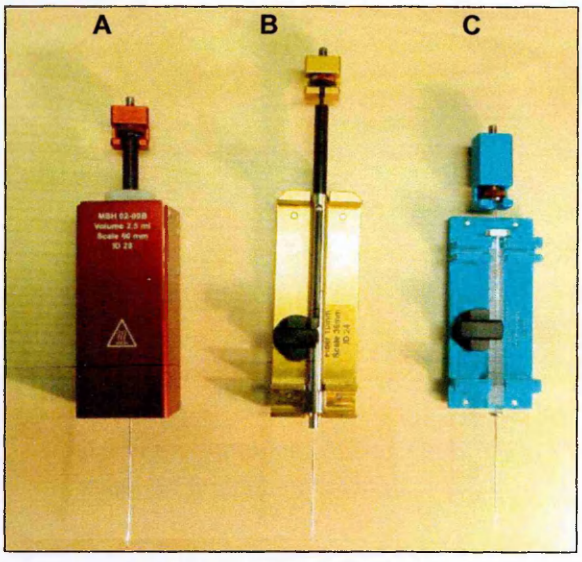

Figure A.9: Inter-changeable GC syringe units which can be interfaced with CTC CombiPal autosampler. A) 2.5 ml static headspace unit B) SPME fibre unit and C) 10 µl liquid injection unit. Headspace, HS-SPME and liquid injection were used in the analysis of THMs while liquid injection was used for HAA analysis.

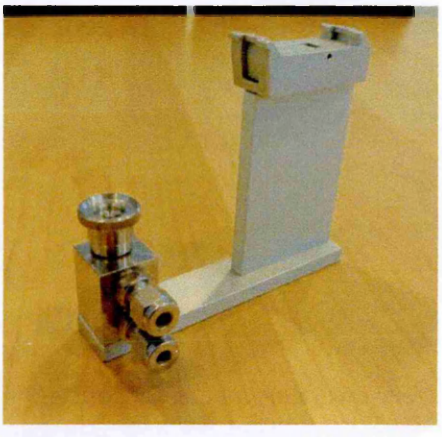

Figure A.10: A flow-through cell which can interfaced on a CTC CombiPal autosampler system for the possible near-real time analysis of THMs.